

**Electrostrictive Polymers for Advanced Sonar
Transducers
(EPAT)**

February 1999 - May 2004

Final Program Report

VOLUME I

**DARPA N00173-99-C-2003
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TABLE OF CONTENTS

ABSTRACT	1
1. Introduction	1
2. Improvement of P(VDF-TrFE) based electrostrictive polymers	3
2.1 The irradiated copolymers:	3
2.1.1 The electromechanical properties of HEEP	5
2.2 P(VDF-TrFE) based terpolymers	8
2.2.1 The electromechanical properties of P(VDF-TrFE-CTFE) terpolymers	10
2.2.2 The electromechanical properties of P(VDF-TrFE-CFE) terpolymers	11
2.2.3 High dielectric constant all-organic composites	12
3. Scale-up and device fabrication	14
3.1 Rolled transducer elements	14
3.2 Continuous irradiation	15
3.3 Transducer element fabrications	17
3.4 Terpolymer scale-up	21
4. Device testing at Penn State	21
4.1 The resonance characterization of the irradiated copolymers	21
4.2 A micro-actuator fabricated from the electrostrictive PVDF based polymers	24
4.3 The flextensional transducer based on the electrostrictive PVDF polymers	25
5. Device testing at Raytheon	27

Abstract

The objective of this DARPA program is to develop high performance electroactive polymers and demonstrate the new polymers for underwater high-power sonar transducers. Through the support of this DARPA program, the electromechanical responses of the high energy electron irradiated copolymer have been improved significantly and PVDF based electrostrictive terpolymers with electromechanical performance better than the irradiated copolymers have been developed. The scale-up of the terpolymer production is current underway and the fabrication techniques for the multilayer transducer elements have been examined. Multilayer transducer elements have been fabricated by manually gluing the layer together and more recently at Electronic Concepts, Inc. by multilayer spiral roll. The preliminary test results on the transducer elements indicate that the transducers have the potential to be used for high power sonar transducer.

1. Introduction

There are three main components in this DARPA program: (1) Improvement of PVDF based electrostrictive polymers, which led to the development of PVDF based terpolymers; (2) scale-up and device fabrication; (3) device demonstration. This final report will summarize the R&D efforts in these three areas. In addition, this DARPA program also contributed to the development of a new class of electroactive polymer – the high dielectric constant all-organic composites in which a high strain can be induced under a relatively low applied field.

In the development of PVDF based electrostrictive polymers, significant progresses have been made through the support of this program. For the irradiated copolymers, there are large increases in the elastic energy density and a large reduction in the applied field. For instance, the field induced strain has been improved from 4.5% with 0.4 J/cm^3 elastic energy density induced under 150 MV/m to 4.5 % with 1 J/cm^3 elastic energy density induced by 90 MV/m. As a result, the electromechanical coupling factor k_{31} is raised to 0.65 which is much higher than that before the program started ($k_{31} \sim 0.3$). More importantly, a non-irradiation approach has been successfully developed. In this program, it has been shown that in P(VDF-

TrFE) based terpolymers, an electrostrictive strain higher than 7% can be induced. The terpolymer has been shown to exhibit a high longitudinal coupling factor $k_{33}=0.55$. Scale-up of the terpolymer to large batch is in progress for the commercialization of the terpolymers. In addition to the high electromechanical responses, one of the advantages of the electrostrictive terpolymers is the low production cost. That is, they can be produced without irradiation. The high electromechanical response will enable them to replace piezoceramics for a broad range of actuators and electromechanical applications.

The scale-up of the films and device fabrication were based on the irradiated copolymers because the amount (~ 0.4 kg) of terpolymer we had is not enough for the fabrication of a device. To produce large quantity high quality irradiated films to be used for the fabrication of devices, we first purchased PVDF-TrFE copolymer at 68/32 mol% composition from Solvay at Belgium. The copolymer is in the research grade quality and contains high gel content. (The copolymer composition which can be converted to ferroelectric relaxor is at VDF/TrFE ratio below 70/30 mol%. These compositions are not commercially available). The films were extruded by K-Tech and it was found that the large amount of pin holes in the extruded films due to the high gel content makes it difficult to produce large size films which can withstand high voltage without breakdown. We then pursued the synthesis of the copolymer at MSI and obtained 70 lbs of 65/35 mol% copolymer. K-Tech had tried to produce extruded films for more than a year. Although they have made progress in improving the extruded film quality, the quality of films produced was not high enough to hold high breakdown field. Because of the time constraints in the program, it was decided that other method of fabrication of thin films should be pursued. In 2002, we learned the capability of ECI (Electronic Concepts, Inc.), a polymer thin film capacitor company, which can produce high quality thin polymer films using drum cast technique. (In fact, this is a standard technique in the polymer thin film capacitor industry to produce polymer thin films which can withstand high electric breakdown field). ECI has produced several rolls of high quality 68/32 mol% copolymer films. Because of time limitation, we could not pursue further in using these films to produce stretched and irradiated films. The regular copolymer films produced by ECI have been rolled into transducer elements which demonstrate the feasibility of using that technique to massively fabricate the transducer elements. Therefore,

all the device elements tested at Raytheon in this program were fabricated at Penn State using a small scale film production and irradiation process.

Several transducer elements have been tested at Applied Research Lab (ARL) of Penn State (during the year 2001) and at Raytheon (in 2002 and 2003). The test results obtained at ARL showed that the device performance at DC bias field less than 40 MV/m is consistent with the prediction based on the polymer electromechanical parameters. At ARL, no test was conducted at above 40 MV/m due to the breakdown of the transducer element. The improved quality of the multilayer transducer elements fabricated at Penn State enabled Raytheon to test these transducer elements to the DC bias field to 85 MV/m. Although the data of the transducer elements at field below 50 MV/m are consistent with the single polymer film data, the electromechanical coupling factor k_{31} showed saturation at fields higher than 50 MV/m, which could be caused by the non-electroded margin in the polymer films used in the transducer element and the low AC field level (the coupling factor may depend on the AC field amplitude). Further design modification is required to eliminate this detrimental effect (such as using k_{33} mode, which is high for the terpolymers).

2. Improvement of P(VDF-TrFE) based electrostrictive polymers

2.1 The irradiated copolymers:

In this program, we investigated copolymers with different compositions and processing conditions, including the annealing procedures and temperatures, irradiation temperatures, dosage, and electron energy. It was found that:

- (a) The field induced strain increases with the VDF/TrFE ratio. In other words, the copolymer with higher VDF content exhibits higher strain response. This is consistent with the idea that the field induced strain originates from the electric field induced conformation change (see figure 1).

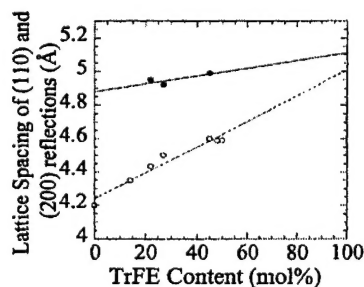


Figure 1

(b) On the other hand, for the copolymers with higher VDF/TrFE ratio, the ferroelectricity becomes stronger and Curie temperature is higher (see figure 2). Therefore, higher dosage is required to convert the copolymer into an electrostrictive polymer. Due to the fact that the irradiation process introduces other effects such as reduction of crystallinity and cross-linking, there is an upper limit in the dosage to be used. Therefore, for the copolymers using the current irradiation and processing technique, the highest VDF/TrFE ratio is 70/30 mol%, beyond which, the copolymers can't be converted into a ferroelectric relaxor with high electrostrictive strain.

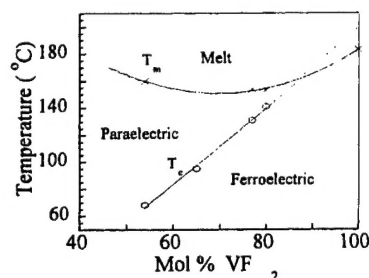


Figure 2

- (c) The electron energy used in the irradiation process also has profound effect. It was found that reducing the electron energy from 2.5 MeV to 1 MeV improved the electrostrictive response. We did not study irradiation with electrons with lower energy than 1 MeV because of the reduction of the penetration depth when the energy of the electron is lowered.
- (d) The temperature at which the irradiation is carried out also has significant effect on the electromechanical responses of the irradiated copolymers. It was found that to achieve the best result, the irradiation should be performed at a temperature above the Curie temperature. On the other hand, high temperature irradiation may cause film deformation. To balance both effects, the irradiation was carried out at a temperature just above the Curie temperature.

In addition to the irradiation conditions, it was found that the annealing treatment prior to the irradiation can also affect the electromechanical response greatly. To obtain high electromechanical response of these films using the irradiation method, the films after stretched have to be annealed, irradiated, and then laminated into bilayer to improve the breakdown field. A new annealing procedure has been developed to continuously anneal these long sheet films (a two step annealing process, i.e., the films were annealed at two different temperatures, first at a lower temperature to release the stress and then at a higher temperature to raise the crystallinity) because the one step annealing process (anneal the film

at one fixed temperature) which has been used for small size films can't be used for annealing of long sheet films. It was found that this two step annealing process has improved the film mechanical quality markedly. In addition, the electromechanical response is also improved. For example, the two step annealed irradiated films exhibit a transverse strain of 4.4% under 85 MV/m field compared with the one step annealed irradiated films of 3.7% strain under 100 MV/m field while the elastic modules of the two irradiated films are the same and the quasi-static coupling factors k_{33} and k_{31} derived based on the electrostrictive strain, the polarization hysteresis loop, and the elastic modulus. Summarized below are the data related to the electromechanical properties of the high energy electron irradiated P(VDF-TrFE) copolymers (HEEIP).

2.1.1 The electromechanical properties of HEEIP

Presented in figure 3 is the field induced thickness strain (longitudinal strain S_3) for the HEEIP where -5% strain is induced under a field of 150 MV/m. The plot of strain versus the square of the polarization yields a straight line, indicating that the response is electrostrictive in nature ($S_3=Q_{33}P_3^2$, figure 3 (b)). Of special interest is the finding that in P(VDF-TrFE) copolymer, large anisotropy in the strain responses exists along and perpendicular to the chain direction, as can be deduced from the change in the lattice parameters between the polar and non-polar phases (see figure 1). Therefore, the transverse strain (the strain in perpendicular to the applied field direction) can be tuned over a large range by varying the film processing conditions. For unstretched films, the transverse strain is relatively small (~1% level under 100MV/m field) while the amplitude ratio between the transverse strain and longitudinal strain is less than 0.33. This feature is attractive for devices utilizing the longitudinal strain such as ultrasonic transducers in the thickness mode, and actuators and sensors making use of the longitudinal electromechanical responses of the material. On the other hand, for stretched films, a large transverse strain (S_1) along the stretching direction can be achieved as shown in figure 3(c), where the transverse strain of more than 4% can be achieved under a field of 85 MV/m.

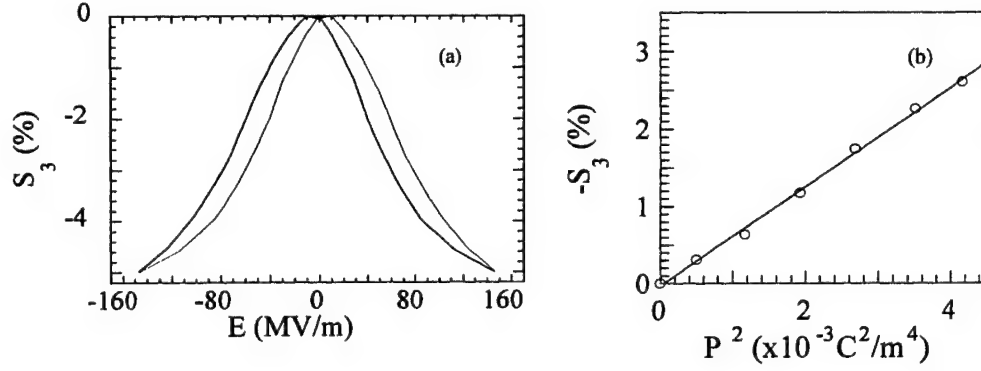


Figure 3 (a)

For electrostrictive materials, the quasi-static electromechanical coupling factor (k_{ij}) has been derived by Hom et al. based on the consideration of electrical and mechanical energies generated in the material under external field:

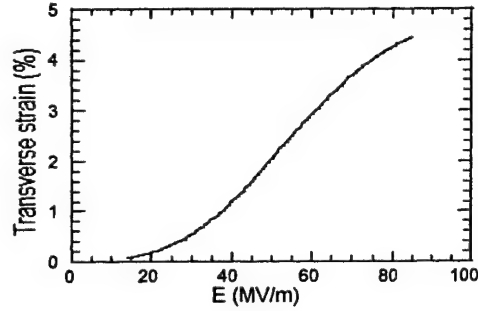


Figure 3 (c)

$$k_{3i}^2 = \frac{kS_i^2}{s_{ii}^D \left[P_E \ln \left(\frac{P_S + P_E}{P_S - P_E} \right) + P_S \ln \left(1 - \left(\frac{P_E}{P_S} \right)^2 \right) \right]}, \quad (1)$$

where $i=1$ or 3 correspond to the transverse or longitudinal direction (for example, k_{31} , is the transverse coupling factor) and s_{ii}^D is the elastic compliance under constant polarization, S_i and P_E are the strain and polarization responses, respectively, for the material under an electric field of E . The coupling factor depends on E , the electric field level. In eq. (1), it is assumed that the polarization-field (P-E) relationship follows approximately:

$$|P_E| = P_S \tanh(k|E|), \quad (2)$$

where P_S is the saturation polarization and k is a constant.

The quasi-static electromechanical coupling factors for the irradiated copolymers are shown in figure 4. Near room temperature and under an electric field of 80 MV/m, k_{33} can reach more than 0.3, which is comparable to that obtained in a single crystal P(VDF-TrFE) copolymer. More interestingly, k_{31} of 0.65 can be obtained in a stretched copolymer, which is much higher

that values measured in unirradiated P(VDF-TrFE) copolymers and, to our knowledge, is the height among all the known ferroelectric, piezoelectric, and electrostrictive polymers. These results are also verified by recent resonance studies in these polymers.

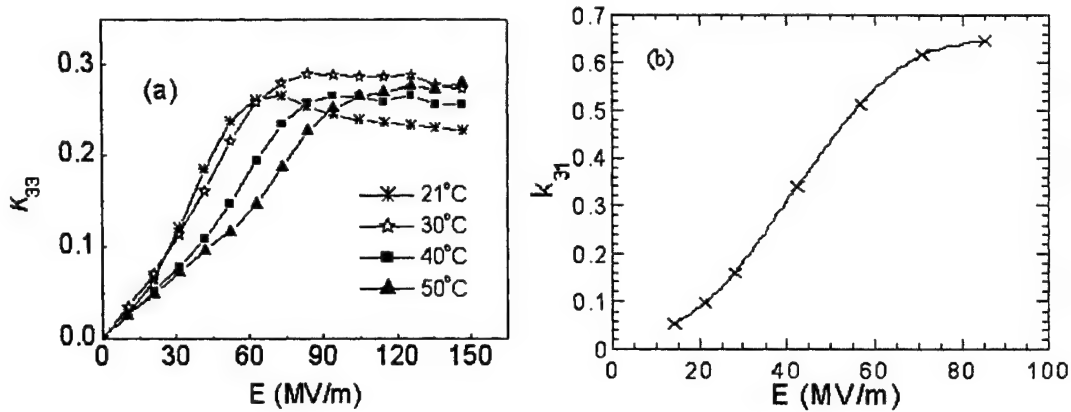


Figure 4 : The electromechanical coupling factors for the irradiated copolymers.

For a polymer, there is always a concern about the electromechanical response under high mechanical load; that is, whether the material can maintain high strain levels when subject to high external stresses. Figure 5 depicts the transverse strain of stretched and irradiated 65/35 copolymer under a tensile stress along the stretching direction. As can be seen from the figure, under a constant electric field, the transverse strain increases initially with the load and reaches a maximum at the tensile stress of about 20 MPa. Upon a further increase of the load, the field-induced strain is reduced. One important feature revealed by the data is that even under a tensile stress of 45 MPa, the strain generated is still nearly the same as that without load, indicating that the material has a very high load capability.

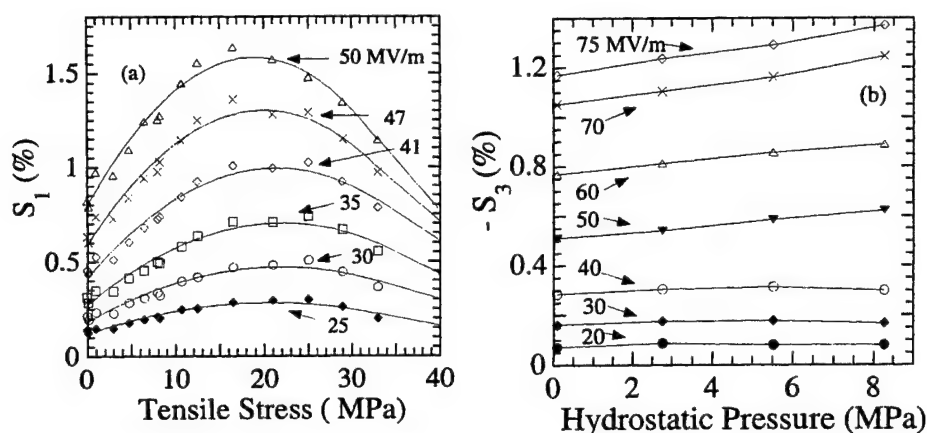


Figure 5: (a) The transverse strain (amplitude) of stretched and irradiated 65/35 copolymer under a tensile stress along the stretching direction and (b) the longitudinal strain of unstretched and irradiated 65/35 copolymer under hydrostatic pressure.

2.2 P(VDF-TrFE) based terpolymers

Three classes of P(VDF-TrFE) based terpolymers were evaluated in this program. The first was P(VDF-TrFE-HFP) (HFP: $-\text{CH}_2\text{-CF}(\text{CF}_3)-$), and then P(VDF-TrFE-CTFE) (CTFE: $-\text{CF}_2\text{-CFCl}-$), and most recent one is P(VDF-TrFE-CFE) (CFE: $-\text{CH}_2\text{-CFCl}-$). To some extent, the effect of the termonomers in the terpolymers can be related to the size of the termonomers. The van der Waals radii of H is 0.12 nm, F is 0.13 nm, and Cl is 0.18 nm. Although all the termonomer sizes are larger than VDF and TrFE monomers, the size of the termonomer is reduced as the termonomer evolves from HFP, to CTFE, and to CFE. It was found that using HFP as the termonomer could reduce the polarization hysteresis and the Curie transition temperature. However, it can't completely remove the room temperature polarization hysteresis and convert the polymer into a relaxor (without Curie transition). Therefore, the strain level in the terpolymer of P(VDF-TrFE-HFP) is not very high ($\sim 2\%$). CTFE as the termonomer can remove the polarization hysteresis and convert the copolymer into a relaxor. However, it requires relatively large mol% (>8 mol%) of CTFE monomer in the terpolymer to realize that. Therefore, the terpolymer of P(VDF-TrFE-CTFE) crystallinity is low (less than 50%) and elastic modulus is not high (~ 0.3 GPa). The field induced strain level is about 5% in this class of terpolymer. The terpolymer with CFE as the termonomer exhibits the best electromechanical responses among the three terpolymers examined. The

mol% of CFE needed to convert the polymer into relaxor is $>6\text{mol}\%$, less than that in the CTFE case. The field induced strain is more than 7% and the longitudinal coupling factor k_{33} can reach 0.55.

The basic mechanism of the introduction of the termonomer randomly into the copolymer chain and crystal lattice is to weaken the ferroelectric coupling and to act as random defect fields to interrupt the macroscopic polarization (the ferroelectricity is in the crystalline region, not amorphous). As a result, the normal ferroelectric polymer is converted into a relaxor with electrostrictive response. Therefore, the effectiveness of the termonomer in converting the polymer into a relaxor will depend on the degree of inclusion of the termonomer in the crystalline lattice. In general, depending on the defect energy of the termonomer in the crystal lattice, the termonomer may be totally excluded from the crystal lattice, which renders the termonomer very ineffective in influence the ferroelectric behavior in the crystalline region, which could be the case of HFP. Due to its very bulkier size in comparison with VDF and TrFE, the defects energy to include HFP could be quite high. As the termonomer size is reduced, the degree for the termonomer to be included in the crystalline region increases. Therefore, it is nature to expect that CFE modified terpolymers exhibits the best electromechanical responses with the lowest amount of termonomer needed. In the semi-crystalline polymer, the introduction of the termonomer in the polymer chain will result in a reduction in the crystallinity. Hence, if possible, the termonomer mol% in the terpolymer should be kept at the lowest level. It was also found that when the size of the termonomer is smaller in comparison with VDF and TrFE, the random introduction of the termonomer in the polymer chains will not result in a significant weakening of the ferroelectric ordering, which is very different from that observed for the terpolymers with the termonomer size larger than VDF and TrFE.

The terpolymers with HFP and CTFE were synthesized using the bulk polymerization method, in which only small quantity of terpolymer can be produced (less than 10 grams per batch) and the terpolymer molecule weight is low. For CFE based terpolymers, although at the beginning, a few compositions were synthesized using the bulk method, for most of the P(VDF-TrFE-CFE) terpolymers, suspension method was used which is a standard method

used in industry to produce copolymers and terpolymers. In this process, we collaborated with Dr. F. Bauer at ISL of France who has developed a reactor which can produce 2 kg of terpolymers per batch. Up to now, the largest batch produced is 800 grams. Table I list the comparison of the molecular weight of these terpolymers (the commercial copolymer is included as a comparison).

Table I. Comparison of the molecular weight of the terpolymers

Sample	Composition	Mn	Mw	MP	Polydispersity
Copolymer	65/35	86092	396580	264004	4.606
ISL-3 (suspension)	CFE 68/32/9	156302	506049	344676	3.237
ISL-4 (Suspension)	CFE 65/35/7	76021	702986	373169	9.247
MC289	CTFE 62.7/33.6/3.7	99735	790653	203929	7.927
MC282	CTFE 64.1/28.8/7.1	51470	242553	137402	4.712
Ter12	CFE 62/38/4	79704	243030	152607	3.049

(2.2.1) The electromechanical properties of P(VDF-TrFE-CTFE) terpolymers

Figure 6 display a typical longitudinal strain data for the terpolymer P(VDF-TrFE-CTFE) (65/35/10mol%). The thickness strain level of the terpolymer is below 4.5% (under 150 MV/m) and the transverse strain is much smaller. We feel that this class of terpolymer is not very attractive for electromechanical applications. On the other hand, the high dielectric constant of the terpolymer is attractive for energy storage devices (capacitors) (see figure 6 (b) for the dielectric constant).

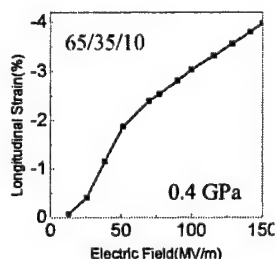


Figure 6(a)

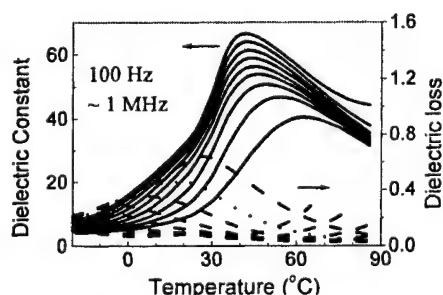


Figure 6 (b)

(2.2.2) The electromechanical properties of P(VDF-TrFE-CFE) terpolymers

Shown in figure 7 is the thickness strain data for a terpolymer P(VDF-TrFE-CFE) 62/38/4 mol% which was synthesized using the bulk polymerization method. It is interesting to note that the terpolymer has a quite high elastic modulus (~ 1.1 GPa at room temperature). Hence, a high quasi-static longitudinal coupling factor k_{33} can be achieved.

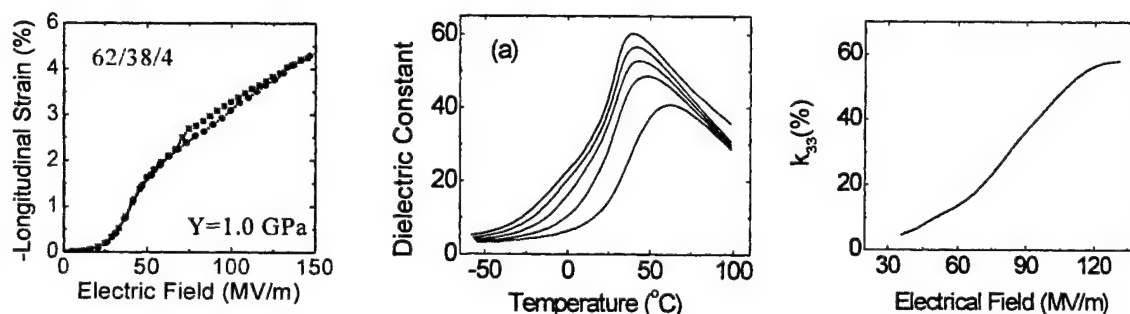


Figure 7

For the terpolymers with higher VDF/TrFE ratio, a higher strain response can be achieved. For instance, shown in figure 8 is the data for P(VDF-TrFE-CFE) 66/34/8.6 mol%. A longitudinal strain higher than 7% can be induced and the transverse strain of the stretched films along the stretching direction can be at 5% (under 150 MV/m). It is interesting to note that the terpolymer exhibits a relatively small volume strain (which is very much different from that of the HEEIP). For example, the volume strain is -0.7% (under 150 MV/m) for unstretched films which is only about 10% of the thickness strain. The elastic modulus of unstretched films is about 0.25 GPa and for stretched films measured along the drawing direction the modulus is 0.35 GPa.

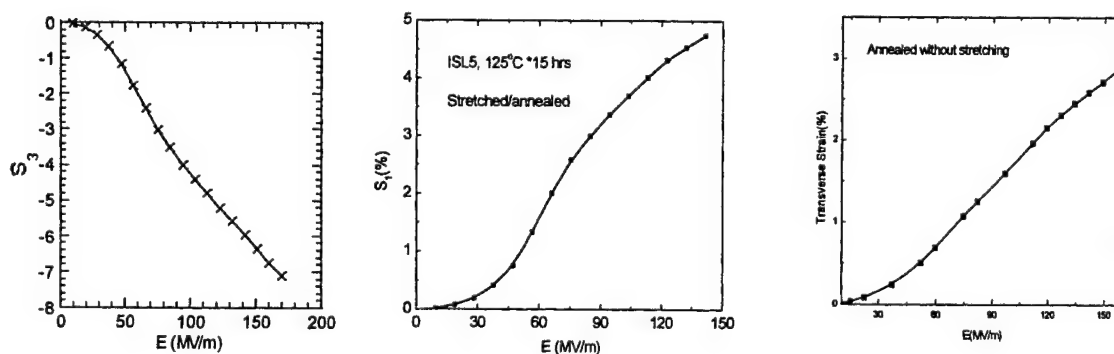


Figure 8

Table II. Summary of the electromechanical properties of the electrostrictive PVDF based polymers and the comparison with other electroactive materials

Materials		Y (GPa)	S_m (%)	Stress (MPa)	$YS_m^2/2$ (J/cm ³)	$YS_m^2/2\rho$ (J/kg)	Coupling factor
Piezo-Ceramics (PZT-5)	S_3	54	<0.2	108	0.11	14.3	0.75
	S_1	61	<0.1	61	0.06	7.8	0.39
PZN-PT Single crystal	S_3	8	1.7	136	1.04	136	0.93
HEEIP (Irrad. Copolym)	S_3	0.5	-5.0	25	0.625	337.8	0.3
	S_1	1.0	4.5	43	1.0	500.0	0.65
P(VDF-TrFE- CFE) terpolymer	S_3	1.1	-4.5,	49.5	1.1	602.2	0.55
	S_1	0.35	7.2 5				

* S_1 is the transverse strain and S_3 is the longitudinal strain. Y is the elastic modulus, S_m is the maximum strain observed. Both the volumetric and gravimetric elastic energy densities are also listed.

In conclusion, through mainly the support of this DARPA support, a new class of the electromechanical material, the PVDF based terpolymer, has been developed. The high strain level (>7%) with a high elastic modulus makes the polymer an attractive choice in many applications where PZT ceramics are used. It is well known that the strain level of 0.2% is far too small for these applications. Table II summarizes the main properties of PVDF based electrostrictive polymers as well as the comparison with other high performance electroactive materials currently in use (PZT ceramics) or under development (PZN-PT single crystals).

2.2.3 High dielectric constant all-organic composites

One of the issues for the further development of the high performance electroactive polymers for DOD applications is how to reduce the applied field level while maintaining the high strain and high elastic energy density. From an energy conservation point of view, the output elastic energy density U_s of an electroactive material cannot exceed the input electric energy density, which is equal to $K\varepsilon_0 E^2/2$. Therefore, a high-input electric energy density is required in order to have a high elastic energy density output. In almost all the current electric-field-activated EAP, the dielectric constant is not very high. Even in the high-energy

irradiated P(VDF-TrFE) copolymers that possess the highest room temperature dielectric constant K among the known electric EAPs, the dielectric constant (~ 60 at 100 Hz) is still far below that in ceramic systems where the dielectric constant in many cases is much higher than 5,000. As a result, a high electric field is required to make up for the low dielectric constant. These considerations point to the need to search for materials and mechanisms that will enhance the dielectric responses significantly in electric-field-activated EAPs, which can improve the coupling factor and induced strain response, and reduce the driving electric field. One of the approaches is based on the dielectric composite concept in which high dielectric constant particulates are blended into a polymer matrix to raise the dielectric constant of the composite. In these new dielectric composites developed here, high dielectric organic solids were utilized for the fillers, which elastic modulus is not very much different from that of the polymer matrix. As a result, the elastic modulus of the new composites is not very much different from that of the polymer matrix. Furthermore, the P(VDF-TrFE) based electrostrictive polymers were chosen for the matrix, which possess a room temperature dielectric constant near 60 and a high electrostrictive strain. Both features are highly desirable for a composite to achieve a high dielectric constant and high field induced strain. In this investigation, copper-phthalocyanine (CuPc) was the high dielectric constant filler (dielectric constant $> 10,000$). The high dielectric constant of CuPc can be explained in terms of the electron delocalization within CuPc molecules. Figure 9(a) presents the dielectric constant and loss of the composites containing 40 wt% of CuPc as a function of the applied field amplitude. As can be seen, under a field of $15 \text{ V}/\mu\text{m}$, the dielectric constant of the composite can reach more than 400 while the dielectric loss is nearly the same as that of the polymer matrix. More interestingly, the composite exhibits a high field induced strain under a much reduce electric field ($\sim 2\%$ strain under a field of $13 \text{ V}/\mu\text{m}$), as shown in figure 9(b). In the figure, the electrostrictive strain from the polymer matrix is also shown for the comparison (as the dashed line). From the elastic modulus (0.75 GPa), the elastic energy density has also be estimated, which is $0.13 \text{ J}/\text{cm}^3$.

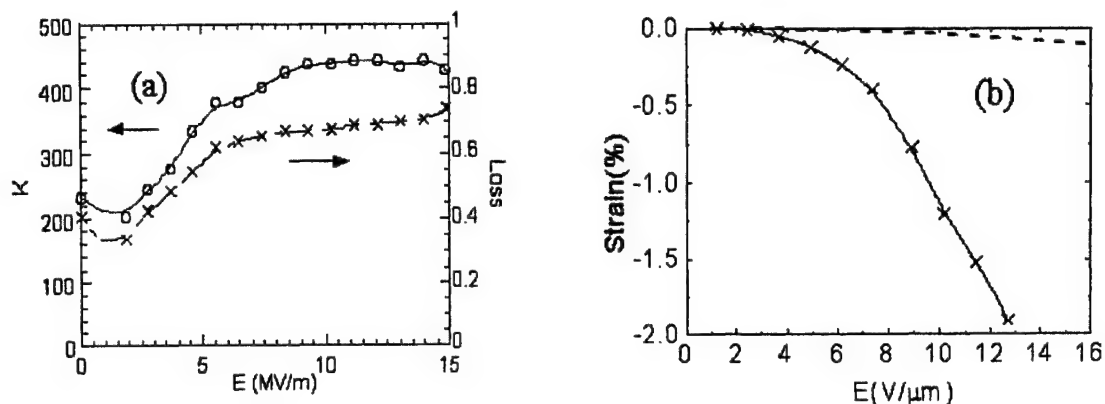


Figure 9: (a) The real part of the dielectric constant (K') and dielectric loss (D) as a function of the applied field amplitude and (b) the strain amplitude as a function of the applied field amplitude measured at room temperature for the composite with 40wt% CuPc. For the comparison, the strain from the electrostrictive P(VDF-TrFE) copolymer at the same field range is also shown (the dashed curve) in (b).

3. Scale-up and device fabrication

3.1 Rolled transducer elements

In the DARPA program, it was planned that the transducer elements to be used at Raytheon will be fabricated using the technique current employed in the polymer thin film capacitor industry: the rolled transducer elements (see figure 10). These rolled multilayer tubes can also be pressed to a plate form. For about two years in the program, the efforts at K-Tech were concentrated on producing large sheets of high quality copolymer thin films using extrusion technique. These films would then be stretched, annealed, and irradiated. The irradiated films would then be metalized and rolled into a transducer



Figure 10

element with proper electric terminations. Although the film quality, in terms of the film uniformity and number of pin holes and defect spots, kept improving during this two year period, the film quality is not high to be used for transducer fabrication. The time constraint of the program forced us to look for other means to produce large quantity of high quality films. In 2002, we started works with Electronic Concepts, Inc, a thin film polymer capacitor

company based in NJ, to produce multilayer rolled transducer elements. At that time, the irradiated copolymers were planned for the fabrication of the rolled transducers. ECI used drum cast method to produce long polymer thin film sheet (to be further processed and irradiated). ECI has produced two batches of drum cast films (each 100 feet long): one (referred to as Batch 1) with thickness 25 μm in summer of 2002 and one (Batch 2) with thickness 45 μm in January 2003 (both of them are 5" width). These films show very high quality (film uniformity and defects such as pin holes) when inspected under polarized optic microscope.

The batch 1 films were uniaxially stretched at Rutgers University which resulted in a film thickness down to 7 to 8 μm . Some of these films were further annealed using the two-step annealing process and irradiated. Because the film thickness is too thin for the device fabrication, we did not pursue annealing and continuous irradiation for the whole roll of the films from that batch. For the films irradiated, the test results indicate that these films possess reasonable electric properties (in terms of the polarization hysteresis and the maximum polarization level) although there are variations of these properties along the film length. The film thickness of the Batch 2 is much thicker than that of the Batch 1. It was expected that with the similar stretching condition, the uniaxially stretched film thickness should be around 15 μm which would be the desired film thickness for the rolled transducer element. When these films were shipped to Rutgers for the uniaxial stretching, due to the change in post-doc in Dr. J. Scheinbeim's group at Rutgers which caused confusion in the experimental procedure of stretching, these films were accidentally annealed which rendered these films not stretchable due to the increased crystallinity. This happened at Feb. 2003. Considering the time limitation in the program, it was decided that these films will not be stretched. Rather, ECI would metalize and then wound these films into rolled transducers.

3.2 Continuous irradiation

We also investigated the possible approach to irradiate the long sheet films so that rolled transducer element can be fabricated using the current multilayer polymer film capacitor fabrication technique. In the first approach we've tested, a long irradiation

chamber (a few feet long and 3" wide) was designed and the long sheet of uniaxially stretched and annealed films were folded along the long-axis of the irradiation chamber. For the current chamber, a 30-40 feet long sheet (3" wide) can be irradiated. The size of the electron source at NIST which are used to irradiate these films is 3"x3". In using such a source to irradiate a chamber of several feet long, the whole chamber was divided into several 3"x3" windows and the irradiation was carried out on each 3"x3" window one by one. Using the current set-up, each day, we can irradiate 5 to 6 3"x3" windows (total 15" – 18" long). The first trial run results are summarized in Table III. Most of the films irradiated show slim polarization hysteresis (as indicated by a small remanent polarization P_r and coercive field E_c and a large P_s , the columns labeled as middle and bottom of two step samples). There are some parts of the film showing large polarization hysteresis (the column labeled as top for two step samples). The cause for that might be due to the temperature non-uniformity in the irradiation chamber. We are working on improving the irradiation chamber. In addition, we also obtained long sheet of extruded films from of 68/32 mol% copolymer from ISL of France which show very slim polarization loops (see extruded film). The only problem for the extruded films from ISL is that they still have gel particles which may cause breakdown when used for bulk devices. These results indicate that this continuous irradiation approach can be used to produce long sheets of irradiated films.

Table III. Long sheet films irradiated at 100°C, 75 Mrad dose

Field Applied = 150MV/m		Sample position during irradiation in the stack of samples		
Sample condition	Polarization	Top	Middle	Bottom
Two Steps	P_s (mC/m ²)	85.78	69.55	78.67
	P_r (mC/m ²)	22.80	7.37	9.32
	E_c (MV/m)	30.67	10.22	11.64
Extruded film	P_s (mC/m ²)	60.68	84.87	86.43
	P_r (mC/m ²)	3.65	3.025	2.84
	E_c (MV/m)	7.96	4.113	9.44

These results demonstrate that the irradiated copolymers can be fabricated into a rolled transducer elements using the multilayer polymer thin film fabrication technique current employed to produce polymer thin film capacitors. The high cost of irradiation, long irradiation time, and irradiation quality control are the problems which can be solved if a dedicated electron source is available for this program. Moreover, the terpolymers which already show better electromechanical responses in comparison with the HEEIPs do not need any irradiation treatment. The experience gained in this program in working with ECI can be directly used in the future for multilayer device fabrications using the electrostrictive terpolymers.

3.3 Transducer element fabrications

In parallel to the efforts of producing rolled multilayer transducer elements which is a process Penn State did not have full control of the schedule (it depended on the schedule of ECI, which can be quite slow sometimes), Penn State has been working on producing small size (3"x3") irradiated films, metalized, and then manually laminated to form a multilayer plate. These plates were then further assembled at Raytheon to form a transducer. Because of the high k_{31} electromechanical coupling factor, the transverse electromechanical mode was used.

At the beginning of the multilayer fabrication, with the aim of improving the breakdown field, the polymer films used in the multilayer plates were glued to form a 30 μm thick bilayer without any electrodes, i.e., each bilayer film was laminated from two non-metalized 15 μm thick films. In this bilayer configuration, pin holes and other defects in one single layer will be likely blocked by the other layer. These bilayer films were metalized and glued to form multilayer plates of 1mm thickness through many steps. (There are 30

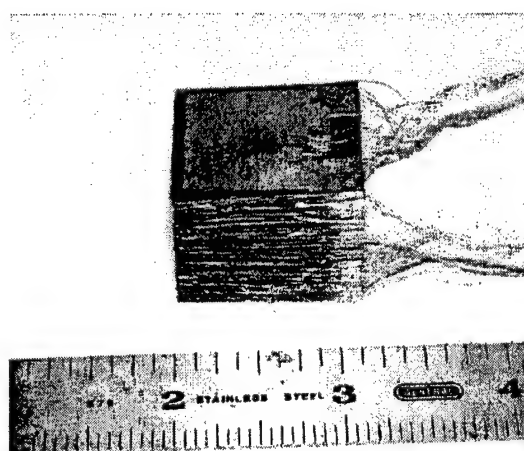


Figure 11

bilayers glued together to form a 1 mm thick multilayer plates, see table IV). Many 1 mm thick multilayer plates (more than 25 pieces of 1 mm thick multilayer plates) were fabricated at Penn State which were assembled into a 1 inch cube for Raytheon to test as a d31 mode transducer (see figure 11). In the tests conducted at Raytheon, it was first found that the electric connection to these multilayer plates was not reliable and these leads connected to the plates often disconnected upon the electric excitation. To improve the electric connection in the high field high strain operation, in the second batch of 1 mm thick multilayer plates (total 33 pieces of 1 mm thick multilayer plates), the electric connections were improved in which several electric leads were connected to one plate and holes were drilled to directly connect these thin wires to each bilayer in the multilayer plates (see figure 12), the holes are filled with silver paint and connected with silver paint and sputtered gold films. Thin silver wires were passing through each hole). These multilayer plates were further laminated together to form a 5 mm thick plates (see Table V). These plates were tested at Raytheon and the results will be given in the section of transducer testing.

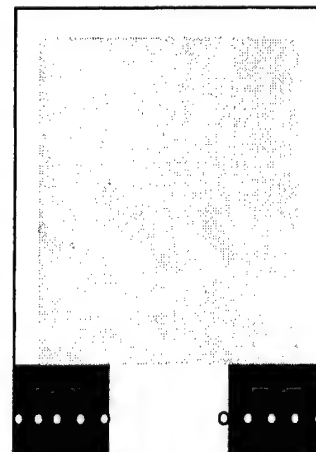


Figure 12. The electric pattern in bilayer films

Table IV: Capacitance of 1 mm thick multilayer plates (measured at 1 kHz)

Plate No.	Capacitance (nF)	Loss	Calculated
1	153.2	0.070	
2	153.4	0.073	
3	155.4	0.070	145.2 nF
4	155.8	0.0717	
5	N/A		
6	149.7	0.0718	
7	156.2	0.074	
8	149.0	0.074	(top layer was peeled off)
9	150.8	0.076	
10	154.0	0.072	
11	164.8	0.068	
12	142.8	0.075	143.7 nF
13	165.0	0.0663	
14	163.9	0.067	
15	166.4	0.0668	
16	161.0	0.072	
17	158.4	0.071	

18	154.8	0.071	
19	151.2	0.074	
20	149.7	0.069	140.67 nF
21	148.7	0.071	
22	153.3	0.066	
23	154.0	0.070	
24	154.4	0.071	
25	163.7	0.071	
26	156.7	0.078	
27	152.6	0.0716	141.69 nF
28	151.6	0.066	
29	150.9	0.059	
30	156.8	0.068	
31	N/A		
32	156.6	0.073	
33	156.0	0.073	140.173 nF

In the test conducted at Raytheon, it was found that the maximum field before breakdown for these multilayer plates is about 50 MV/m above which the plates electrically breakdown. The coupling factor k_{31} under a DC bias field of 50 MV/m is 0.24, which is close but a little smaller than that deduced from the quasi-static data. One of the possible reasons might be that the DC bias field is not high enough. From figure 4, to reach higher coupling factor state, a higher DC bias field seems to be required which means that the breakdown field of these multilayer plates should be raised quite significantly (to above 80 MV/m). Another possibility is that the AC field amplitude is too low in these tests.

Table V. Capacitance of the 5 mm thick plates

Plate No.	Capacitance (nF)	Loss
A	791	0.085
B	806	0.081
C	765	0.087
D	753	0.083
E	703	0.082
F	609	0.086 (only 4 mm thick)

In order to improve the breakdown fields so that the transducer elements can be operated at higher DC bias field, the polymer film process at Penn State was modified:

- (a) All the films are now cast in a class 100 clean room to significantly reduce the dust particles in the polymer films produced.

- (b) The films after the irradiation are visually inspected for any possible pin holes and defects which can cause electric breakdown in these films. Any polymer films with visible defects are removed.
- (c) The films after metallization are tested under 120 MV/m field to make sure that these films can withstand high field strength.
- (d) Multilayer fabrication is carried out in clean bench (class 100, which is current available to us).

These are the steps taken at Electronic Concepts Inc. in producing multilayer polymer thin capacitors with high field reliability. It was found that after these steps, we can use even single layer polymer films to fabricate multilayer plates which can withstand field of more than 85 MV/m. Three multilayer plates of 1 mm thick which consists of about 50 layers of 20 μm thick single layer films laminated together using a soft glue (glue layer thickness is in between 2 to 3 μm). These multilayer plates were tested in December, 2002 and found that they could withstand fields higher than 90 MV/m for more than one hr in air without breakdown. The final breakdown in these multilayer plates was caused by the air breakdown. Therefore, the results indicate that for future multilayer plates, if the field is below 90 MV/m and the test and device operation are conducted in an insulation oil to eliminate air breakdown, these multilayer plates can be used reliably. Shown in figure13 are the 1 mm thick multilayer element fabricated at ECI.

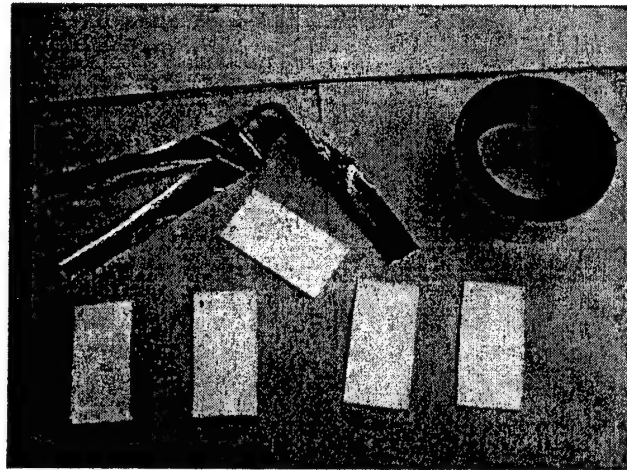


Figure 13

These results demonstrate that the irradiated copolymer films can be fabricated to multilayer elements to be used in transducers for operation at fields up to 85 MV/m. From the electromechanical property data of the irradiated copolymer measured at 1 Hz and under 85 MV/m field, the polymer can produce a strain of more than 4% with an elastic energy density more than 1 J/cm³ and coupling factor of 0.65. Furthermore, the results from the resonance

study and from the MEMS actuator indicate that the electrostrictive PVDF based polymers can be operated at frequencies to more than 100 kHz with the coupling factor the same as that deduced from the quasi-static data (figure 4).

3.4 Terpolymer scale-up

The most important accomplishment of this DARPA program is the discovery and development of PVDF based electrostrictive terpolymers, which are produced from polymer synthesis without any further irradiation treatment and exhibit high induced strain ($>7\%$ strain) and elastic energy density ($\sim 1 \text{ J/cm}^3$). The terpolymers will be an important family of the actuator materials for a broad range of applications. In collaboration with ISL at France, we are in the process of scale-up the production of terpolymers using the suspension polymerization method, which is a standard polymerization method used in industry to produce PVDF based copolymers. Currently, the ISL reactor can produce 1 kg per batch (it takes about 5 hrs to synthesize one batch).

4. Device testing at Penn State

4.1 The resonance characterization of the irradiated copolymers

All the transducers designed and tested in this program were based on the transverse electromechanical mode (k_{31} mode). As shown in figure 4, the stretched and irradiated copolymer exhibits a high quasi-static k_{31} (~ 0.65). For practical devices, because of high electric field, the polymer layers used need to have non-electroded edges to prevent the electric breakdown at the edges which will affect the coupling factor. Therefore, a series resonance tests were conducted to examine the effect of the unelectroded margins. The electric impedance

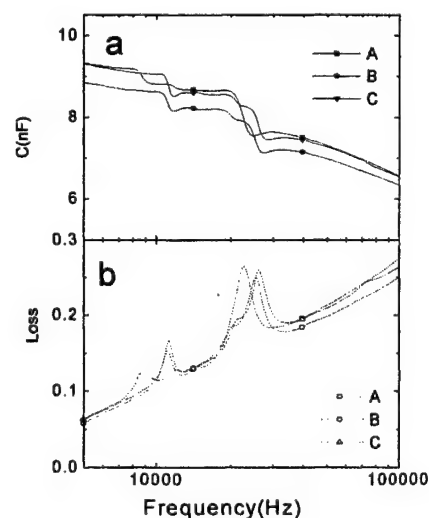


Figure 14

curves for the films with different unelectroded margins are shown in figure 14 and from the data, the coupling factor k_{31} can be deduced as listed in Table VI.

It is obvious that as the unelectroded margins are reduced, the measured k_{31} increases. In the tests to be conducted for the device and single layer testing, the unelectroded margin is about 2 mm on all the sides. The electric

impedance curves for the single sheet films ($\sim 20 \mu\text{m}$ thick) under different DC bias field are shown in figure 15, from the resonance peak positions, the coupling factor k_{31} can be deduced. On the other hand, for a resonance device with a high loss, the coupling factor can be extracted from the resonance curve by fitting the data over the relevant frequency range. The results from the two methods are shown in figure 16 along with that deduced from the quasi-static data (for this sample, the quasi-static coupling factor k_{31} is 0.45 under a 100 MV/m field). The results indicate that the coupling factors from the three methods are consistent with each other. At the DC bias field above 50 MV/m, k_{31} from the resonance curve is less than that deduced from the quasi-static data. One of the possible explanations is that the coupling factor deduced from the resonance curves is the small AC signal value (AC field $< 0.1 \text{ V}/\mu\text{m}$) while the one from quasi-static data is for the large AC field case (AC field $> 30 \text{ V}/\mu\text{m}$), which may explain the lower coupling factor in the Raytheon data. For a ferroelectric relaxor, it is well known that the coupling factors and other piezoelectric coefficients will depend on the applied field amplitude. The data indicate that by increasing the driving field amplitude, the coupling factor k_{31} may be increased.

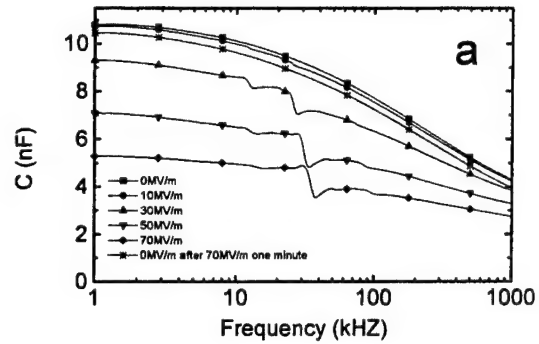


Figure 15

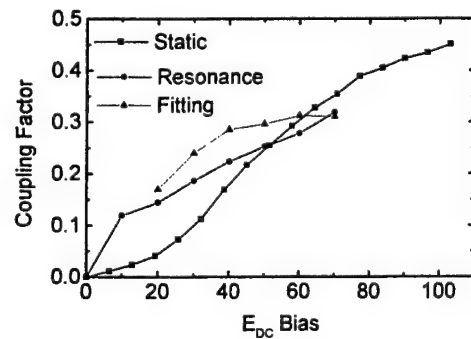


Figure 16

Table VI. The effect of non-electroded margins on the measured k_{31} coefficient

Sample	Geometry : $t=22.5\mu\text{m}$, $L_e=20.8\text{mm}$, $W_e=40.3\text{mm}$ for all of them	Resonance frequencies f_s		k_{31}	
		\perp stretch direction	// stretch direction	\perp stretch direction	// stretch direction
A	$L_{\text{total}}=28.6\text{mm}$ $W_{\text{total}}=61.4\text{mm}$	8688	22460	0.109	0.168
B	$L_{\text{total}}=28.6\text{mm}$, $W_{\text{total}}=44.8\text{mm}$	11198	23930	0.123	0.173
C	$L_{\text{total}}=25.7\text{mm}$ $W_{\text{total}}=44.8\text{mm}$	11134	26564	0.149	0.186

In the fabrication of multilayer transducer elements, glue was used to laminate the films together. It is expected that these glue layers will affect the coupling factor as well, especially for the transverse electromechanical effect in which the glue layer is mechanically directly coupled to the strain. To reduce the glue layer effect, the glue to be used should be elastically much more compliant than that of polymer layers and the glue layer thickness should be as thin as possible. For the tests conducted here, the glue layer thickness is $1\mu\text{m}$ (compared with the polymer layer thickness of $20\mu\text{m}$). The modulus of the glue layer is ~ 2 to 3GPa which is a little bit higher than the stretched copolymer films ($\sim 1\text{GPa}$). The data for the single layer and

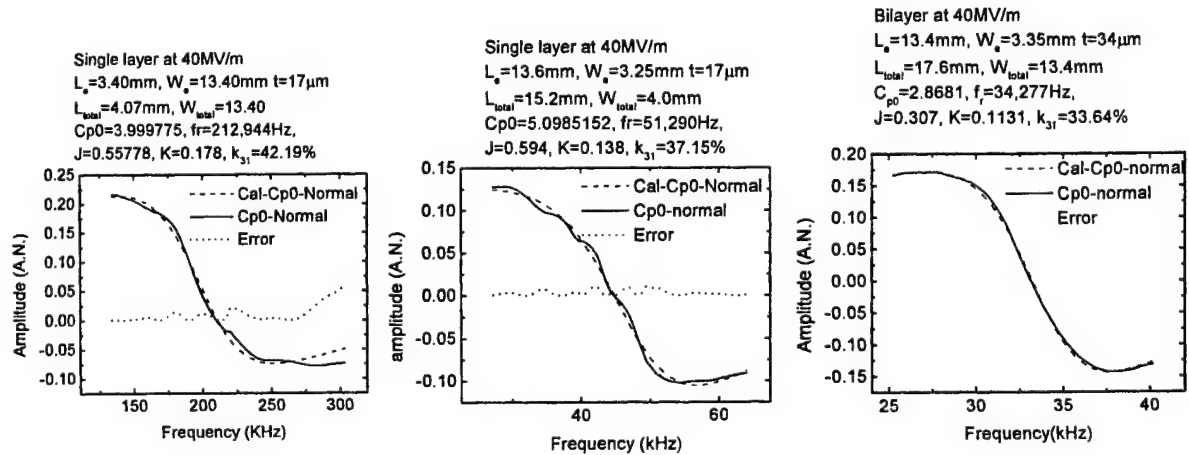


Figure 17

bilayer are shown in figure 17. The results indicate that the glue layer does have some effect in reducing the coupling factor k_{31} as expected and the effect is not significant (reduced from 0.37 to 0.33, a 10% reduction).

4.2 A micro-actuator fabricated from the electrostrictive PVDF based polymers

In order to assess the high frequency performance of the electrostrictive PVDF based polymers developed in this program, a polymer micro-actuator (PMAT) was fabricated and tested (this part of the work was mainly supported by an NIH grant). A schematic of the PMAT is shown in figure 18. PMATs with two different L_0 were investigated: $L_0=1$ mm and $L_0=0.5$, (thereafter refer to as PMAT1 and PMAT0.5). As shown in figure 19, under a field of 100 MV/m and measured at 100 Hz, PMAT1 can generate a displacement of near 50 μm and PMAT0.5 near 20 μm , which are much larger than the MEMS actuators fabricated using other active materials such as piezoceramics. The small device allows for the

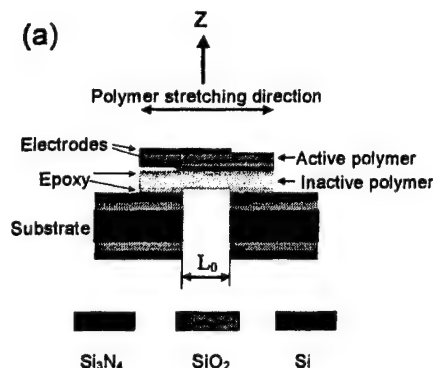


Figure 18

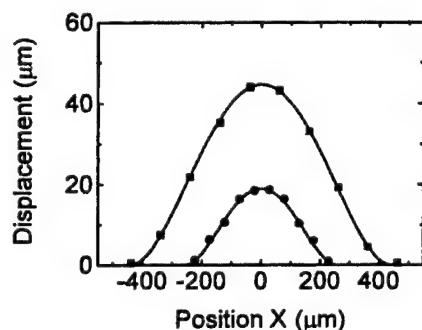


Figure 19

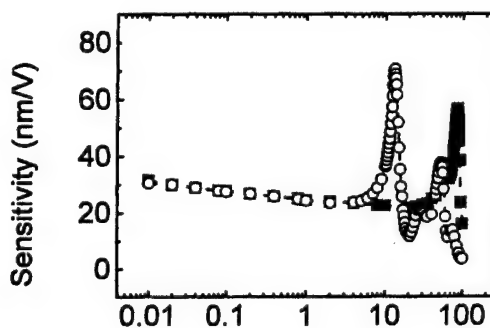


Figure 20

characterization of the frequency response to high frequency. As demonstrated in figure 20, the strain response does not show large reduction with frequency even up to 100 kHz, indicating

that the electrostrictive PVDF based polymer developed in this program is suitable for high frequency operation. (This work was performed in 2001).

4.3 The flextensional transducer based on the electrostrictive PVDF polymers

In late 2001, in collaboration with the Applied Research Laboratory at Penn State, we fabricated a flextensional transducer using the multilayer plate from the electrostrictive PVDF polymer. The use of the flextensional transducer for the test was based on the fact that at that time we still had not find a method to fabricate large quantity multilayer plates and ONR was interested in knowing the device performance. This type of transducers can be used for Navy Sonar applications at frequencies below 2 kHz. For this transducer, the irradiated copolymer in the transverse electromechanical mode has $k_{31}=0.45$ under a field near 100 MV/m (which is different from the two step annealed samples). The multilayer plate (1 mm thick) was fabricated from 31 μm thick bilayer films. The flextensional transducer was tested at ARL water tank to obtain both TVR (transmitting-voltage response) and FFVS (free-field voltage sensitivity). In the TVR measurement, the pressure generated by the transducer as a projector under different DC bias and AC fields was measured by a

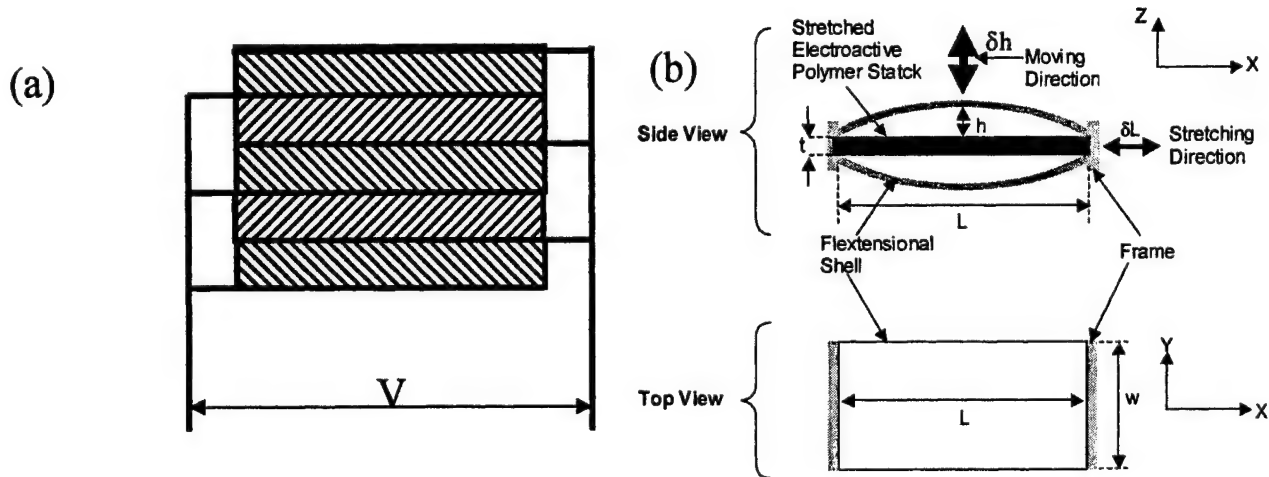


Figure 21

hydrophone placed 1 meter away from the transducer. The data are presented in figure 21 for TVR. A broad resonance was observed centered at 1.7 kHz. From the resonance peak, the

mechanical quality factor, Q_m , of the projector operated in water could be calculated by Eq. (3),

$$Q_m = \frac{f_r}{f_h - f_l} \quad (3)$$

where f_r is the resonance frequency, while f_h and f_l are the half-power frequencies which can be determined from the -6 dB points in the TVR curve. For this transducer, the mechanical Q is $Q_m=1.55$. The TVR near the resonance is 122.5 and 123.2 (dB re 1 $\mu\text{Pa/V}$ @1m) for the device under DC bias fields of 1000 V and 1500 V, respectively.

For electrostrictive material such as the irradiated P(VDF-TrFE) copolymers used here, an effective piezoelectric state can be induced by a DC bias electric field. Thus, the material can also be used to sense acoustic signals. To evaluate the receive response of the transducer, the FFVS was obtained and is presented in figure 22. For a DC bias of 1500 V (50 MV/m), the FFVS was -177.5 (dB re 1V/ μPa) near the resonance frequency.

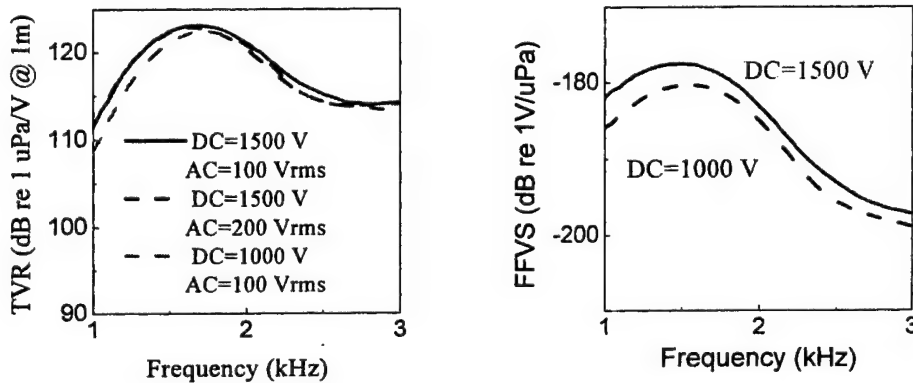


Figure 22

As an electrostrictive material, the electromechanical response increases with DC bias field if the DC field is far below the saturation field, which is the case for the DC fields used here as can be seen from figure 1. The observed increase in both TVR and FFVS is consistent with this.

In addition to the relatively high TVR at such a low frequency, the flextensional transducer was also capable of generating high source level (SL) because its high electric field limits. For the flextensional transducer investigated here, an AC voltage of 1500 volts is equal to an electric field of $48 \sim 50 \text{ V}/\mu\text{m}$ which is much smaller than the high field limitation in the polymer film. For instance, if a voltage of 1500 volts is applied to the transducer (50 MV/m AC field) and a linear response is assumed for the EAP stack, the SL could reach more than 185 dB re $1 \mu\text{Pa}$ @1m.

5. Device testing at Raytheon

Please see the following section.



Integrated Defense Systems

<p>Electrostrictive Polymer</p> <p>Acoustic Transducer (EPAT)</p> <p>Final Report</p>
<p>Submitted Under: 1625RSC-ONR-2003</p>
<p>Prepared For: Qiming Zhang Materials Research Laboratory The Pennsylvania State University</p>
<p>Prepared by Raytheon Integrated Defense Systems Acoustics Engineering Section, MS N17 1847 West Main Road Portsmouth, Rhode Island 02871-1087</p>

September 30, 2003

TABLE OF CONTENTS

1.0	INTRODUCTION.....	1
1.1	Objective and Approach	1
1.2	Comparison of Electrostrictive Polymer and Conventional Ceramic.....	1
1.3	Other team members	2
2.0	TRANSDUCER DESIGN & ANALYSIS.....	3
2.1	Finite Element Transducer Analyses	3
2.1.1	Flexing Disk.....	3
2.1.2	Cymbal.....	5
2.1.3	Bulk Mode Cube	6
2.2	Spiral-wrapped Cylinder	7
2.2.1	Finite Element Analysis	7
2.2.2	Conventional Analysis	8
3.0	TESTING.....	11
3.1	Transducer Test Housing	11
3.2	High Voltage Biasing Electronics.....	14
3.3	Tests of Flexing Aluminum Disk.....	15
3.4	Cube 1	15
3.4.1	Initial Tests, in Air	16
3.4.2	In-water Tests.....	17
3.5	Individual Plates.....	18
3.5.1	Construction.....	18
3.5.2	Electrical Tests on Plates, in Air.....	18
3.5.2.1	150-layer Plates.....	18
3.5.2.2	Thin Sheets.....	21
3.6	Cube 2	24
3.6.1	In-water Tests, Housing Filled with Gas	24
3.6.2	In-water Tests, Housing Filled with Fluorinert Liquid	26
3.7	Tripod Conceptual Design	27
4.0	SUMMARY OF PROGRAM RESULTS	28
5.0	REFERENCES.....	29

LIST OF FIGURES

Figure 1: (a) Electrostrictive polymer sample, (b) Conventional ceramic shapes	2
Figure 2: Finite element flexing disk model	4
Figure 3: Performance predictions for flexing disk	4
Figure 4: Finite element model of cymbal design	5
Figure 5: Performance predictions for cymbal and flexing disk.....	6
Figure 6: Finite element depiction of bulk cube design (22 layer configuration)	7
Figure 7: Finite element model of spiral-wrapped cylinder.....	8
Figure 8: (left) Hoop stress magnification ratio, (right) in-water resonance frequency	10
Figure 9: (left) Maximum efficiency, (right) Figure of Merit by weight.....	10
Figure 10: (left) TVR at resonance, (right) effective coupling factor.....	11
Figure 11: EPAT flexing disks, (left) aluminum, (right) fiberglass	12
Figure 12: Transducer test housing (3 views).....	12
Figure 13: Engineering drawing of transducer test housing	13
Figure 14: In-water test configuration	13
Figure 15: Schematic of electrical biasing circuit used in EPAT measurements	14
Figure 16: Transmitting Voltage Response for 0.040" aluminum flexing disk.....	15
Figure 17: EPAT bulk mode Cube 1	16
Figure 18: In-air tests on Cube 1 at 20 Vpp, 500 Vdc	16
Figure 19: Cube 1 as assembled in test housing	17
Figure 20: Admittance, Cube 1 in air, in test housing	17
Figure 21: Plate electroding scheme	18
Figure 22: Plate admittance ($Y = G + jB$), in air	19
Figure 23: Curves derived from admittance for Plate "B"	20
Figure 24: Plate "C" data at higher bias fields.....	20
Figure 25: Data summary for Plate "C" in air, 10 Vrms excitation.....	21
Figure 26: Data summary for thin sheets at room temperature	22
Figure 27: Thin sheet S4 at room temperature (plain) and 40°C ("Hot").....	23
Figure 28: Coupling vs temperature and bias for Sheet S8	23
Figure 29: Stages of Cube 2 transducer assembly	24
Figure 30: Cube 2 acoustic data (gas filled, 25 MV/m bias, 40 Vrms drive).....	25
Figure 31: Vertical and horizontal beam patterns.....	25
Figure 32: Cube 2 in fluid-filled housing configuration.....	26

LIST OF TABLES

Table 1: Comparison of electrostrictive polymer and conventional piezoceramic.....	1
Table 2: Parameters used in initial finite element analysis.....	3
Table 3: Performance predictions of flexing disk element designs	5
Table 4: Performance prediction comparison between cymbal and flexing disk	6
Table 5: Length of active material required.....	9

1.0 INTRODUCTION

The purpose of the Electrostrictive Polymer for Acoustic Transducers (EPAT) program was to study new electromechanically active materials being developed in the Materials Research Laboratory at The Pennsylvania State University (MRL/PSU), with an emphasis on evaluating underwater sound transducers made using these new materials. Results of the acoustical evaluations were fed back to the material researchers to guide further development.

1.1 Objective and Approach

The main objective of the study was to demonstrate, via electrical and acoustical testing, the performance advantages and drawbacks of the new EPAT material. The approach was to design, fabricate, and acoustically evaluate devices to demonstrate critical transducer properties. Methods used were math modeling of new concept designs to select candidate approaches, then fabrication and test of selected designs. Math modeling was initially done using material properties supplied by MRL/PSU, and later with properties measured at Raytheon on test samples. New measurement apparatus and test techniques were required to fully characterize both raw EPAT material and devices made from it.

1.2 Comparison of Electrostrictive Polymer and Conventional Ceramic

Electrostrictive polymer is believed to have great promise in underwater acoustic transducers because of its high strain capability, ruggedness, and near-ideal ρc match to water. Table 1 compares properties of electrostrictive polymer and conventional piezoceramic. Although a few items in the list are similar, there are major differences in most quantities. The engineering challenge is to discover how to fashion acoustic transducers to exploit the favorable qualities of electrostrictive polymer material.

Table 1: Comparison of electrostrictive polymer and conventional piezoceramic

Preliminary EPAT Characteristics

- Requires DC Bias
- Optimal in 31 mode
- $d_{31} = 260 \text{ pm/V}$
- Low Young's Modulus
- Low Density, Mass
- Good impedance match with seawater
- Physical properties nonlinear as a function of temperature
- High capacitance ($3 \mu\text{F}$)
- High dissipation (0.07)
- Max V_{AC} Field > 2000 V/mil

Standard PZT-4 Characteristics

- Requires No DC Bias
- Optimal in 33 mode
- $d_{33} = 285 \text{ pm/V}$
- High Young's Modulus
- High Density, Mass
- High impedance mismatch with seawater
- Physical properties nearly linear as a function of temperature
- Low capacitance (610 pF)
- Low dissipation (0.004)
- Maximum V_{AC} Field = 8~10 V/mil

Figure 1 shows a comparison between a sample sheet of electrostrictive polymer (a) and some common ceramic shapes (b). The electrostrictive polymer sample shown in (a) is about one inch square. The polymer material goes through numerous processes in order to exhibit electrostrictive properties. First the polymer is stretched along one plane to align the molecules. This stretching also strengthens the material significantly. The resultant long sheets of stretched material, approximately 15 μm thick, are then cut into smaller sizes and sputtered gold electrodes, 350 to 400 \AA thick, are applied to both sides. Next the electrostrictive properties of the sheets are enhanced by exposing the material to high energy electron beam irradiation. Finally the thin sheets are sandwiched together using a very thin layer of epoxy, and electrical leads are attached with conductive epoxy.

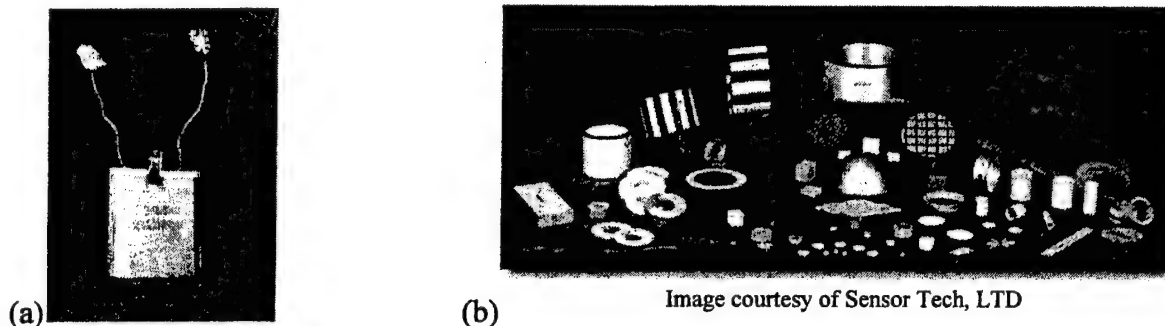


Figure 1: (a) Electrostrictive polymer sample, (b) Conventional ceramic shapes

1.3 Other team members

- Materials Research Laboratory, The Pennsylvania State University (MRL/PSU)
- Ktech
- Rutgers University
- Naval Undersea Warfare Center, Newport (NUWC Div NPT)
- ONR, DARPA (sponsors)

2.0 TRANSDUCER DESIGN & ANALYSIS

The first stage of the program involved a modeling exercise in which preliminary values for the material parameters were used to develop conceptual designs of acoustic sources. Material parameters, shown in Table 2, included Poisson's ratio, shear modulus, Young's modulus, piezoelectric coefficients, and permittivities. The values used reflected what was known about this and similar materials at the time the initial models were created.

Table 2: Parameters used in initial finite element analysis

Poisson's ratio:	Piezoelectric Matrix (pm/V)
$\nu_{21} = 0.16$	$[d] = \begin{bmatrix} 0 & 0 & -190 \\ 0 & 0 & 2 \\ 0 & 0 & 220 \\ 0 & 0 & 0 \\ 0 & 2 & 0 \\ 2 & 0 & 0 \end{bmatrix}$
$\nu_{31} = 0.36$	
$\nu_{32} = 0.26$	
Shear Modulus GPa:	
$G_{12} = 2.6$	
$G_{21} = 2.4$	Permittivity Matrix (pC/m ²)
$G_{31} = 1.0$	
Young's modulus GPa:	
$E_1 = 2.5$	
$E_2 = 2.1$	$[e] = \begin{bmatrix} 67.3 & 0 & 0 \\ 0 & 67.3 & 0 \\ 0 & 0 & 67.3 \end{bmatrix}$
$E_3 = 0.9$	

2.1 Finite Element Transducer Analyses

A variety of element designs were created using the ANSYS finite element modeling software, modified to handle piezoelectric materials. The element designs include a bimorph flexing disk, a cymbal configuration, a spiral-wrapped cylindrical stack, and a bulk mode cube. More detail about each type is given below.

2.1.1 Flexing Disk

The first design analyzed with the finite element method was a bimorph flexing disk, a device which uses two square pieces of EPAT material sandwiched on opposite sides of a circular flexible membrane. The two active EPAT layers are driven electrically out of phase to produce flexure of the membrane. The configuration was modeled with two different materials for the flexible membrane, aluminum and G10 fiberglass composite. These two materials were chosen for availability and for their differing flexure properties. A picture of one quarter of the modeled structure is shown in Figure 2. The overall diameter of the device is 2.5 inches. Predicted transmitting voltage response curves are shown in Figure 3. The peaks of the TVR curves shift in frequency as a function of the stiffness of the material used as the bending membrane. With a stiffer layer the resonant frequency increases. A complete summary of the performance characteristics is included in Table 3.

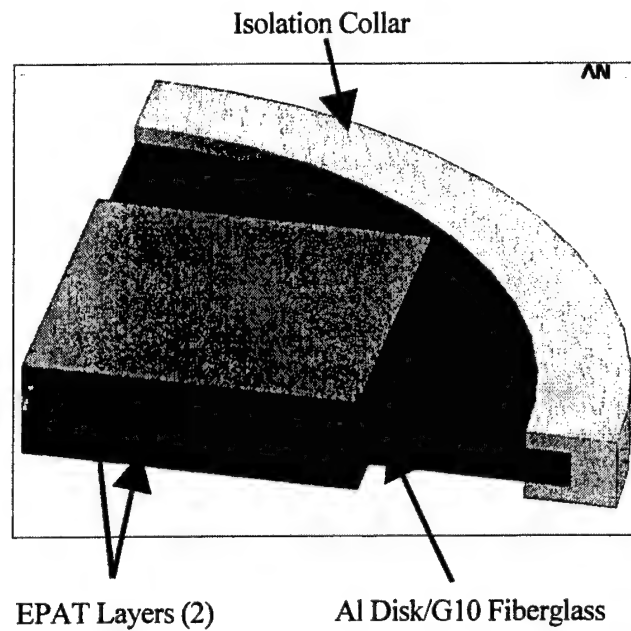


Figure 2: Finite element flexing disk model

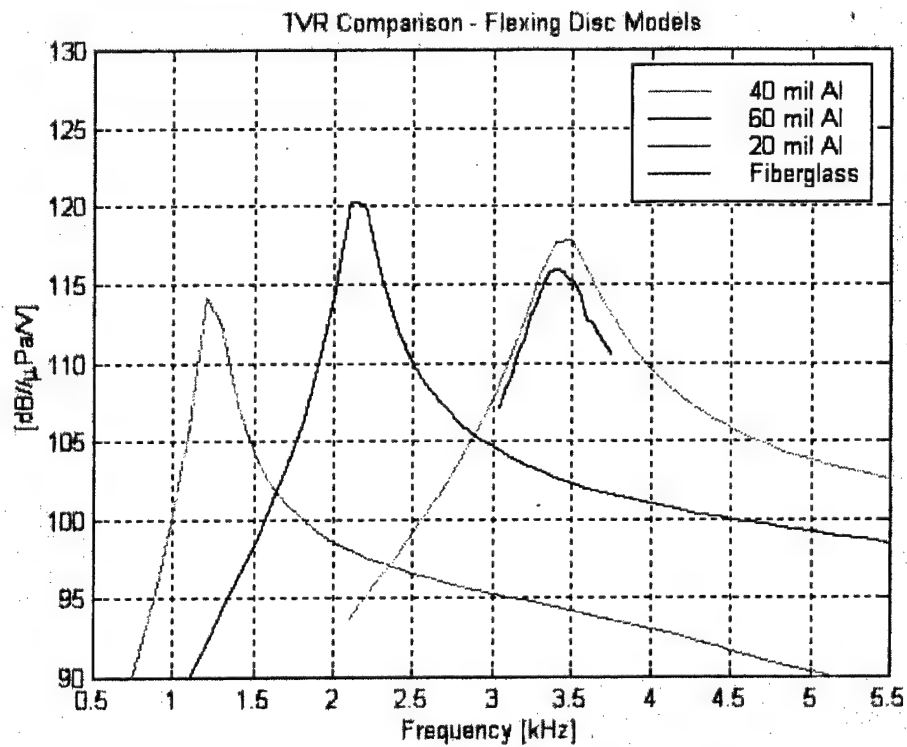


Figure 3: Performance predictions for flexing disk

Table 3: Performance predictions of flexing disk element designs

Element	20mil Aluminum	40mil Aluminum	60mil Aluminum	40mil G10
Peak TVR Level (dB/ μ Pa/V)	114.2	117.9	116.0	120.3
Peak TVR Level Freq. (Hz)	1200	3525	3400	2100
-3dB/ μ Pa/V Bandwidth (Hz)	214.03	385	330	210
Resultant Q	5.6	9.2	10.3	10.0
SL (300 Vac)	163.8	167.4	165.5	169.8
DI (dB) -- 1.8" diameter	0	0	0	0
Mass (kg)	0.005	0.007	0.010	0.006
Volume (m ³)	2.82E-06	3.65E-06	4.49E-06	3.65E-06
Acoustic Power (watts)	2.019E-01	4.723E-01	3.022E-01	8.133E-01
FOM _{mass}	5.88	1.99	0.90	6.63
FOM _{vol}	10.66	4.01	1.92	10.61

2.1.2 Cymbal

The second design analyzed with the finite element method was a cymbal configuration. This type is similar to the flexing disk except the active material is enclosed within a thin-walled envelope. The exterior of the cymbal design was modeled as a flexible plastic membrane with a thickness of 0.05 inches. Again, two square sheets of EPAT material were mounted on opposite sides of a central flat plate, however in this design the two active EPAT layers are driven in phase to create purely planar extension of the central plate. The center plate was a 0.040 inch thick aluminum plate, the same as in the flexing disk design. A picture of the modeled cymbal design is shown in Figure 4. Similar dimensions as the flexing disks were used, and again the overall diameter of the unit was 2.5 inches. The predicted transmitting voltage response of the cymbal is shown in Figure 5 along with the same measure for a flexing disk configured with the 0.040 inch thick aluminum plate. The cymbal design produced a higher resonant frequency than the flexing disk, but at lower output levels. A summary of performance characteristics for both designs is given in Table 4.

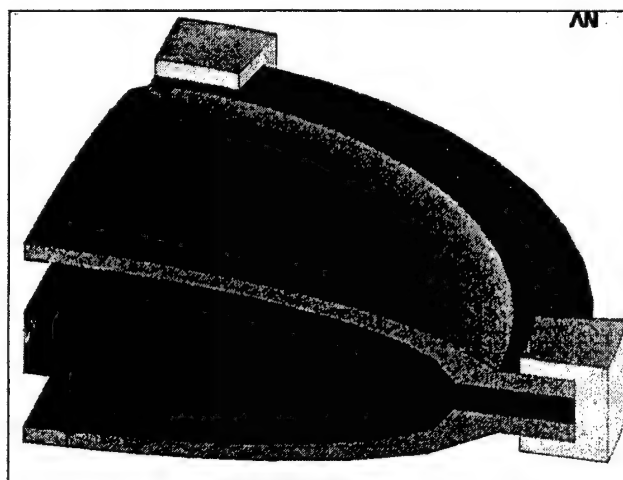


Figure 4: Finite element model of cymbal design

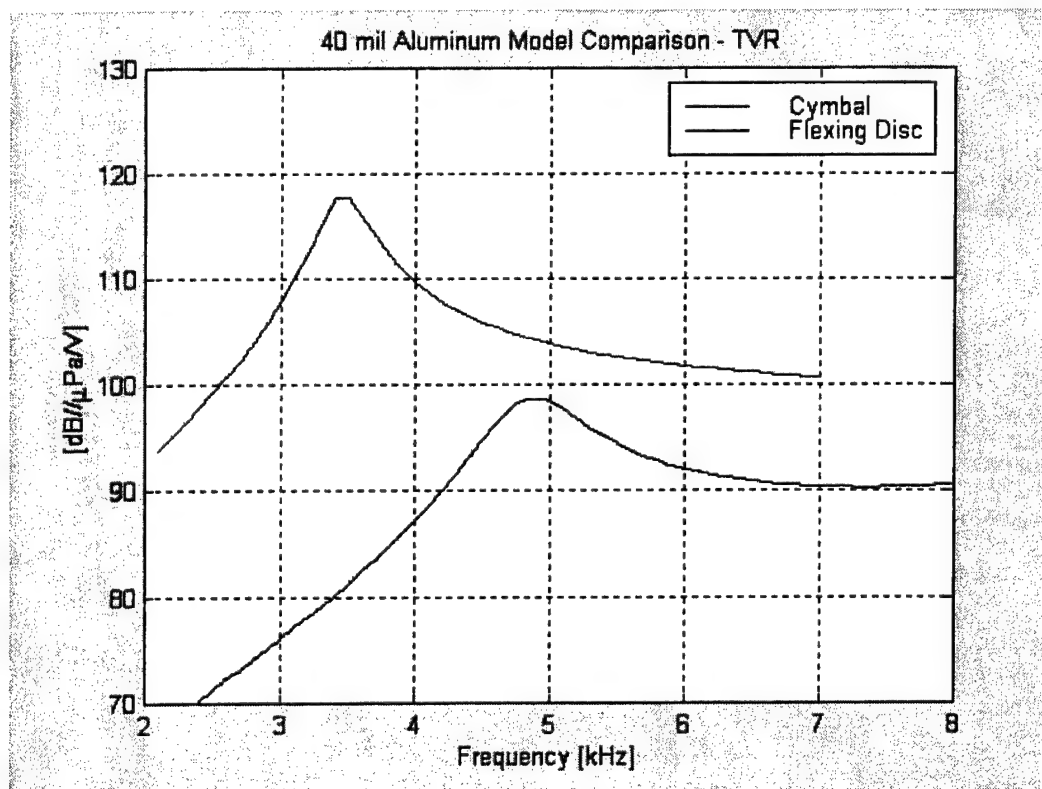


Figure 5: Performance predictions for cymbal and flexing disk

Table 4: Performance prediction comparison between cymbal and flexing disk

Element	40mil Aluminum Cymbal	40mil Aluminum Flexing Disc
Peak TVR Level (dB/μPa/V)	98.6	117.9
Peak TVR Level Freq. (Hz)	4950	3525
-3dB/μPa/V Bandwidth (Hz)	890	385
Resultant Q	5.6	9.2
SL (300 Vac)	148.1	167.4
DI (dB)	0	0
Mass (kg)	0.007	0.007
Volume (m ³)	3.65E-06	3.65E-06
Acoustic Power (watts)	5.498E-03	4.723E-01
FOM _{mass}	0.027	1.99
FOM _{vol}	0.055	4.01

2.1.3 Bulk Mode Cube

The third design analyzed consisted of a solid block of EPAT material. The largest configuration of this type is shown in Figure 6. The cube is a stack of 22 EPAT sheets wired in parallel. Two smaller cube configurations were also investigated, 10 sheets and 15 sheets. The color scheme in Figure 6 shows the different materials used in the model: aqua indicates the plastic acoustic window, blue the EPAT material, and red an isolation backing of Corprene (a cork-rubber

mixture). The overall dimensions of the EPAT cube are shown in the figure, and the thicknesses of the plastic window and the Corprene layer are 0.125 inches and 0.230 inches, respectively. Due to an undetermined modeling error the modeled transmitting voltage responses for the three stack configurations were not valid (invalid frequency range, abnormally high Q's), so analysis results are not presented.

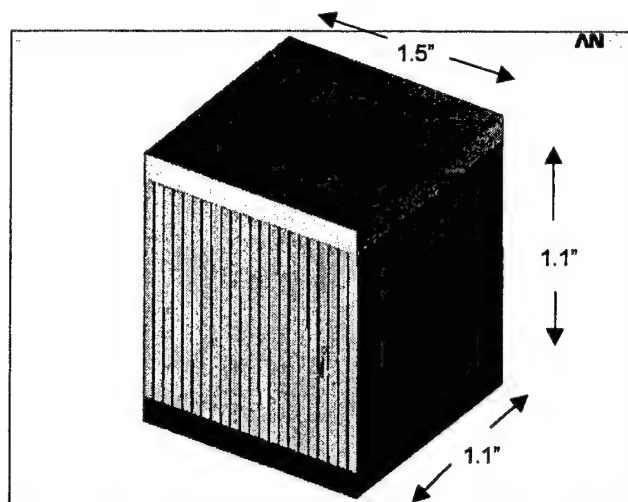


Figure 6: Finite element depiction of bulk cube design (22 layer configuration)

2.2 Spiral-wrapped Cylinder

2.2.1 Finite Element Analysis

Another design investigated with the finite element method was a spiral-wrapped cylinder. In this concept a long strip of EPAT material is rolled around a solid core to create a hoop-mode cylindrical projector. A picture of this design is shown in Figure 7. The EPAT material is colored red and the core material light blue. The outside dimensions of the cylinder are given in the figure, the diameter of the core is 0.60", and the thickness of each wrap layer is 0.04".

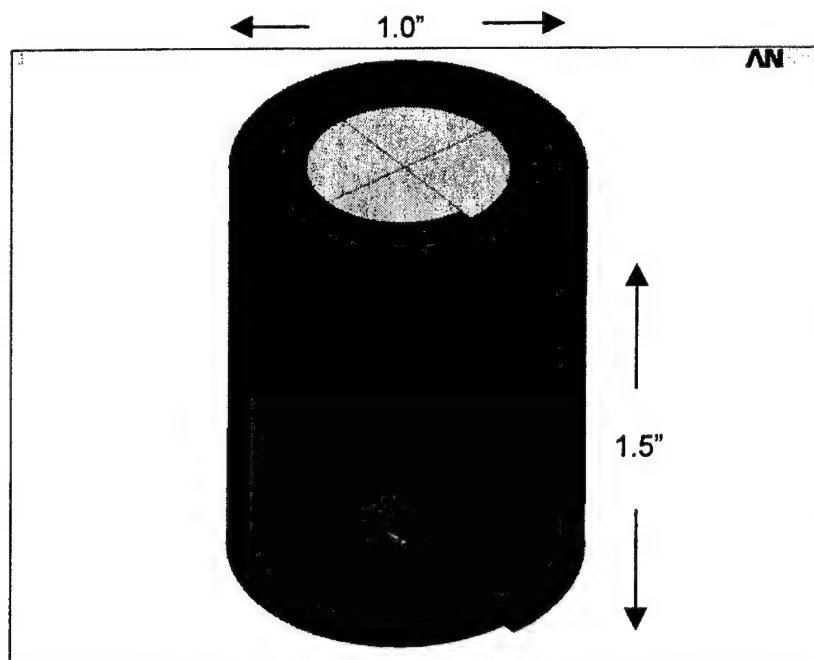


Figure 7: Finite element model of spiral-wrapped cylinder

The first FEA modeling attempt for the cylinder produced an acoustic response similar to the previous results for the 22-layer bulk cube (abnormally high-Q resonance), and were thought to be invalid. This model was not pursued further.

2.2.2 Conventional Analysis

In addition to the FEA analysis reported in the previous section, an analytical model of the spiral wrapped cylinder was also developed. Use of the analytical model gave insight into the effect of varying materials and dimensions and suggested optimal shapes and material choices.

The basic approach and assumptions in the model were as follows:

- Two concentric cylinders: an outer one of active material, an inner one of inert material, with continuity of radial and tangential displacements at the interface
- Thick-wall stress distributions used in both cylinders
- Outer wall of the active cylinder in contact with the acoustic medium
- Ends of both cylinders and inside wall of the inner cylinder isolated from the acoustic field
- Active cylinder consisting of many thin layers wired in parallel, simulating a spiral wrap
- Active materials considered: EPAT @ 25 MV/m bias, Channel 5800 ceramic
- Inert materials considered: Nothing, Lucite, G-10 fiberglass, aluminum, steel

After validating the model for a single layer case (typical air-backed ceramic cylinder), families of designs were studied with varying inert cylinder sizes and material. The length and OD of the outer cylinder were arbitrarily fixed at 75 and 49 mm respectively (aspect ratio of 3:2), the thickness of active layers was set at 30 μm (the usual EPAT dimension), and the number of active layers varied with the space available as the diameter of the two-cylinder interface ("ID" in the next three figures) was varied.

The inside diameter of the inner cylinder defined the "core" and took on four values:

- Zero (solid core)
- One-half the interface diameter (1/2 core)
- One-quarter the interface diameter (1/4 core)
- Equal to the interface diameter (no core)

Transducer performance metrics evaluated were

- Ratio of maximum hoop stress in the active material to external hydrostatic pressure
(The location of the maximum hoop stress can vary within the active cylinder depending on inert material choice and interface diameter.)
- In-water resonance frequency
- Maximum TVR (at resonance)
- Effective coupling factor
- Maximum electro-acoustic efficiency
- Figure of Merit (acoustic output power divided by resonance, Q, and total weight). Output power was evaluated at 565 Vrms, the maximum possible drive voltage for 800 V bias.

The required quantity of active material was also calculated. This was the same for all active materials and core fillings and is tabulated below, expressed as the length of ribbon wrapped in the spiral.

Table 5: Length of active material required

Interface Diameter (mm)	Length of strip (ft)
0	103
4	102.5
8	100.5
16	92
32	59
38	41
44	20

Results from preliminary runs with different inert materials showed a preference for the softer materials, so only the Lucite backing results are presented here (see Figure 8 through Figure 10). The following discussion gives an interpretation of these modeling results.

A large hoop stress magnification factor means that tangential (T_1) stresses in the active material are large for a given hydrostatic pressure, which is undesirable for deep operation. Figure 8 shows this metric is largest for thin outer shells (large ID), however all other indicators favor thick outer shells (small ID), and in that region the stress differences between core sizes and IDs disappears. In general a no-core, all-active solution is best (lowest frequency, largest TVR, coupling, efficiency, and FOM). But if a core is needed, to eliminate wrinkling or buckling on the inner wrap layers, then winding the spiral on a small, thin Lucite bobbin appears to be nearly as good as having no core.

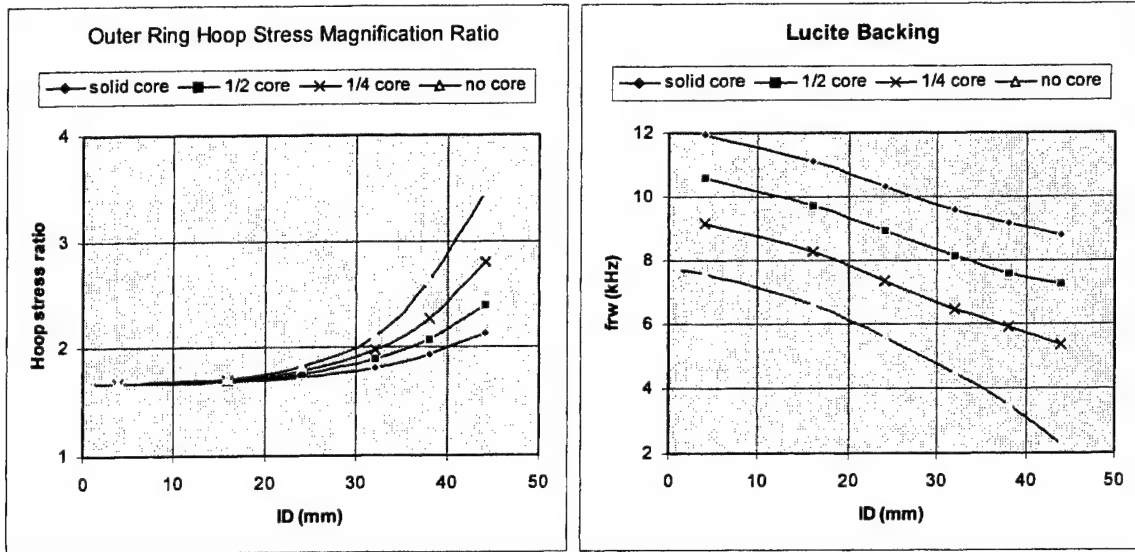


Figure 8: (left) Hoop stress magnification ratio, (right) in-water resonance frequency

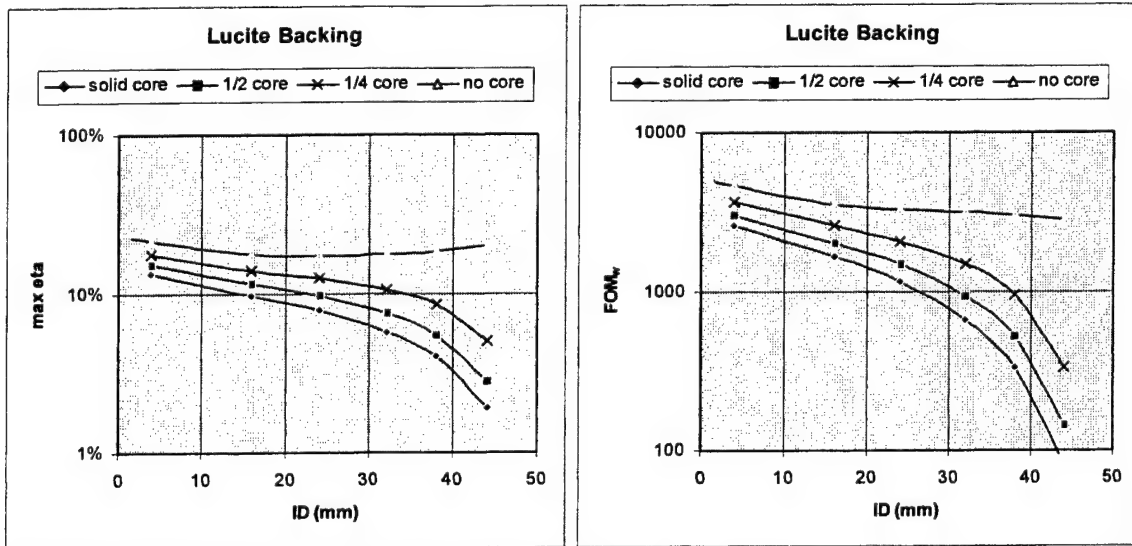


Figure 9: (left) Maximum efficiency, (right) Figure of Merit by weight

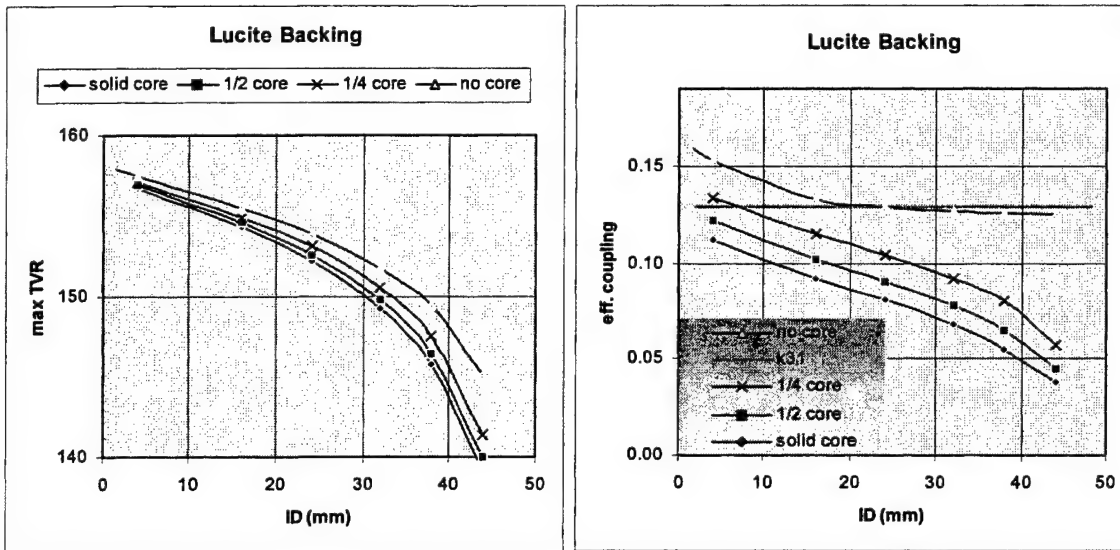


Figure 10: (left) TVR at resonance, (right) effective coupling factor

In the right-hand graph of Figure 10 the horizontal line is k_{31} , the material coupling coefficient used in the model. This value should be the upper limit of effective coupling for the transducer, however $k_e > k_{31}$ in some cases indicating a flaw in the model (or at least in the coupling determination). Since the trends in these graphs seem reasonable, the overall conclusions of the tradeoff study are considered valid.

3.0 TESTING

3.1 Transducer Test Housing

After reviewing the preliminary models the transducer configuration which appeared to have the most potential (and could be assembled rather quickly) was the flexing disk design. EPAT sheets were received from MRL/PSU and two units were assembled: one with a 0.040" thick aluminum center membrane and one with a 0.040" thick G10 center membrane. These two configurations can be seen in Figure 11. The EPAT was bonded to the aluminum and the G10 sheets with contact cement.

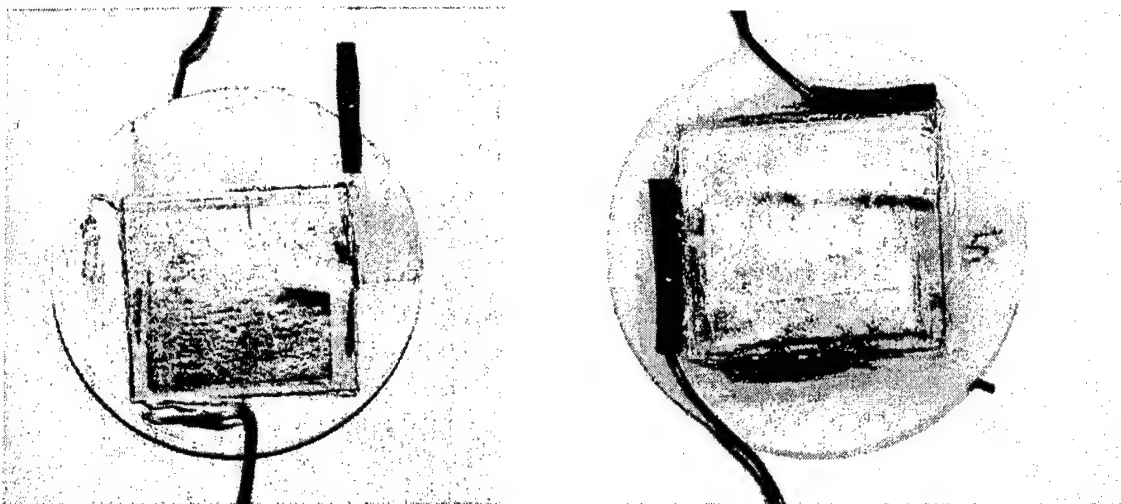


Figure 11: EPAT flexing disks, (left) aluminum, (right) fiberglass

The active subassemblies were then placed into the transducer test housing which is described in the next two figures. The left hand picture in Figure 12 shows the top side in which the white circle is the radiating aperture; the middle picture shows the backside of the transducer, including the electrical terminals; the right hand picture is the top view again, but with the acoustic window removed so placement of the EPAT material can be seen. After the active element was wired and assembled into the transducer housing, the unit was filled with Fluorinert liquid to provide for pressure compensation and additional electrical insulation. The housing was not to be submerged below 8 ft in our tests so pressure compensation was unnecessary, but filling the housing with fluid provided better coupling to the water. Figure 14 is a schematic of the testing configuration showing how the two EPAT layers on opposite sides of the plate were driven electrically out of phase and how the dc bias voltage was introduced into the circuit. The dc biasing circuit is described in the following section.

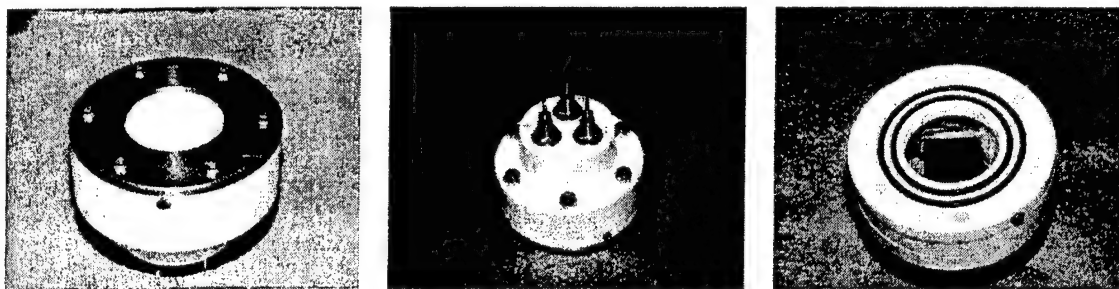


Figure 12: Transducer test housing (3 views)

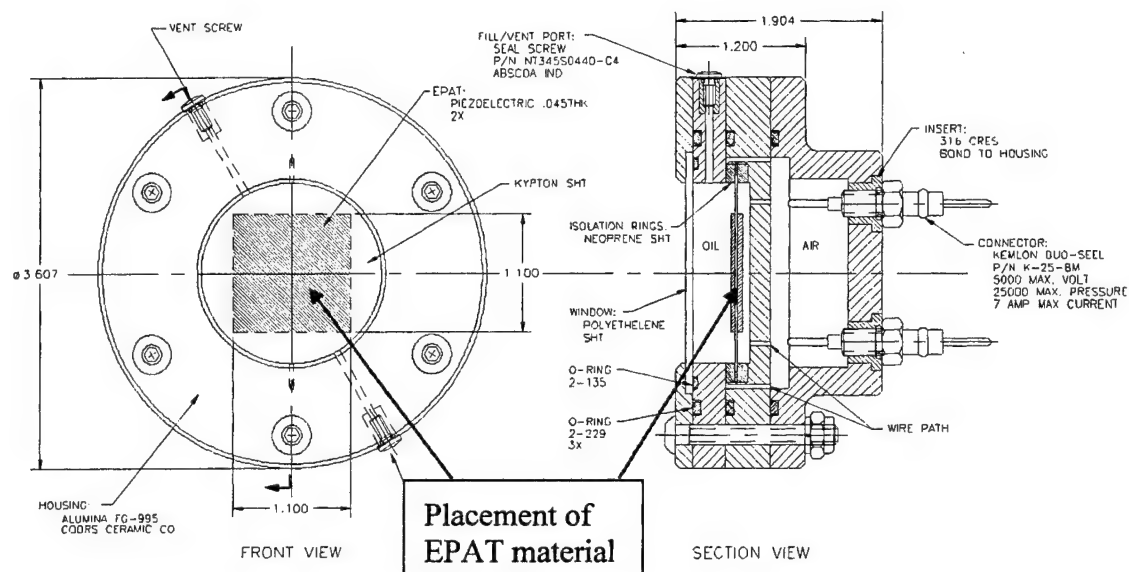


Figure 13: Engineering drawing of transducer test housing

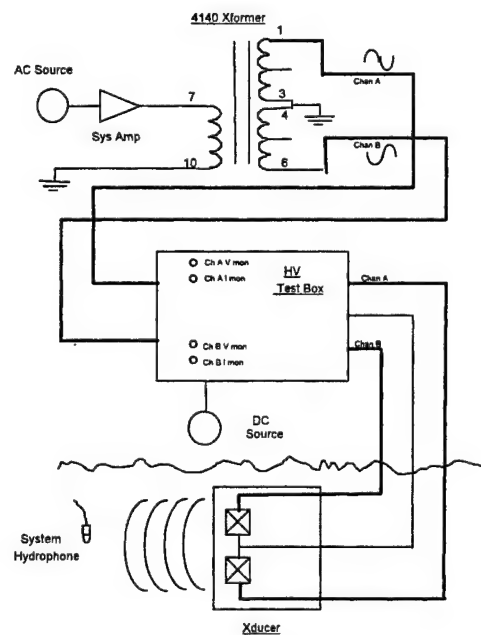


Figure 14: In-water test configuration

3.2 High Voltage Biasing Electronics

Figure 15 is a schematic of the two-channel biasing circuit used during EPAT measurements. The two voltage sources on the left represent signal generators driving each side of the flexing disk unit in out-of-phase operation. The $1\ \mu\text{f}$ blocking capacitors in series with each electrical source isolate dc voltage from the ac signal generators. The two sides of the EPAT transducer are depicted as shunt R,C combinations C15/R8 and C25/R28. The source on the right side is the dc supply, isolated from the ac circuits by $1\ \text{M}\Omega$ resistors R4 and R24.

Resistors R27 and R29 are small values for sensing drive currents. These were later replaced by inductive current transformers. The H-shaped branch formed by elements R25/C24/R26/C21, and its companion in the lower half of the circuit, are capacitive voltage dividers for measuring drive signals. One of these was later replaced by a high voltage probe. Only one channel of the biasing box is normally used since only the flexing plate test transducer needed two-channel out-of-phase drive.

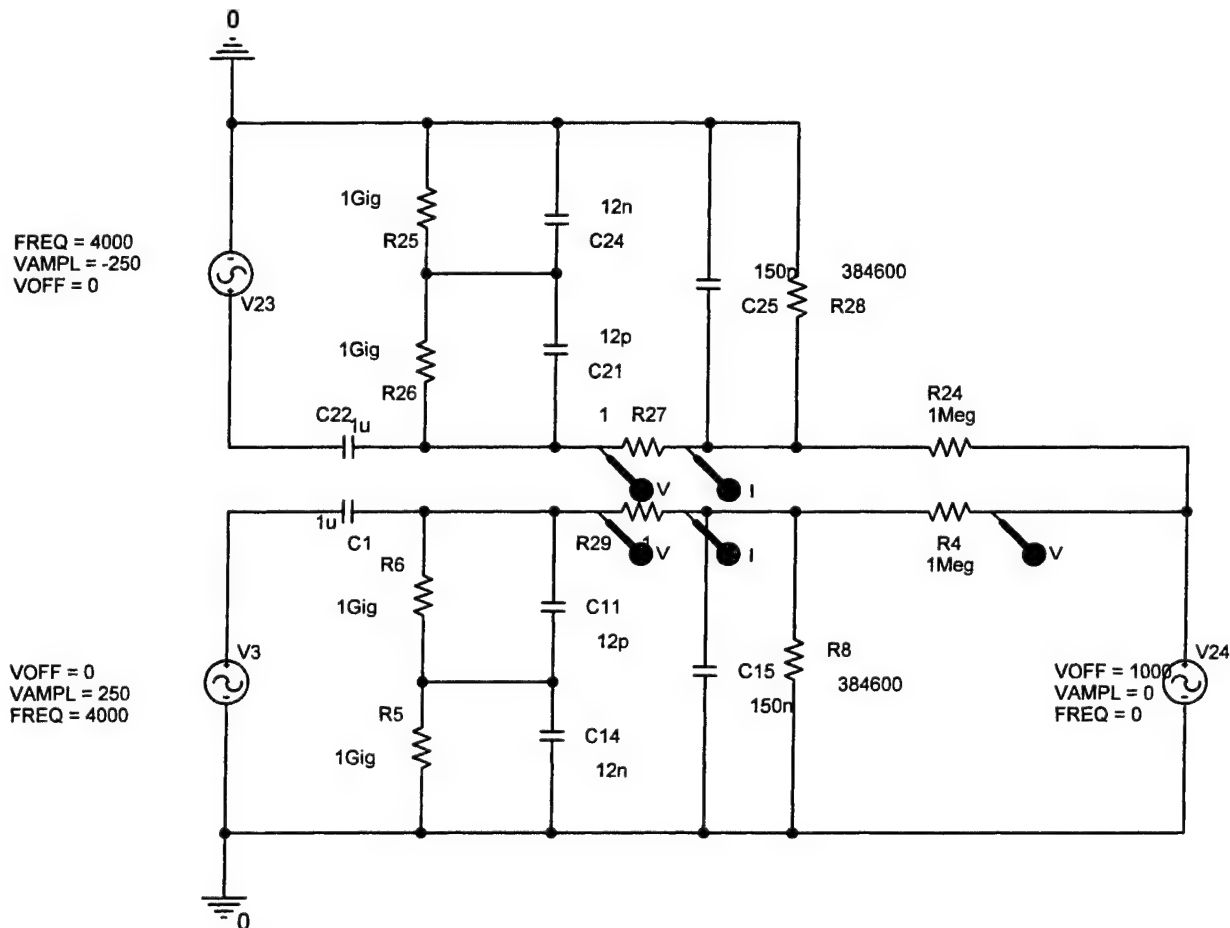


Figure 15: Schematic of electrical biasing circuit used in EPAT measurements

3.3 Tests of Flexing Aluminum Disk

Fabrication of the flexing disk configuration, including bonding of the EPAT material to the aluminum and the fiberglass disks, assembly of the transducer housing and filling with Fluorinert liquid were completed. The unit was tested in air to confirm that the electrical contacts had survived the assembly procedure, then it was submerged to a depth of approximately 8 ft in the Raytheon Acoustic Test Facility tank.

Initial ac drive levels of the aluminum flexing disk were kept low while the dc bias level was varied between 1000 Vdc and 1500 Vdc. As testing continued the drive levels were increased slowly while bias levels were held between 1000 and 1500 Vdc. Figure 16 shows the resulting transmit voltage response curves. The left-hand graph shows the lower Vac drive levels and the right-hand side gives the higher (100 Vac) drive levels. Comparing results in the same frequency range as the models given above, the levels and profiles do not match very well in level. Most likely the test housing or the active material, or both, contributed higher losses than expected causing the actual output levels to be much lower than predicted. However, at higher frequencies the TVR had peaks at 26.5 and 38.9 kHz with levels of 130 and 132 dB// μ Pa/V, respectively. The in-air impedance around these frequencies shows no distinctive resonances, suggesting that these response peaks are housing cavity resonances.

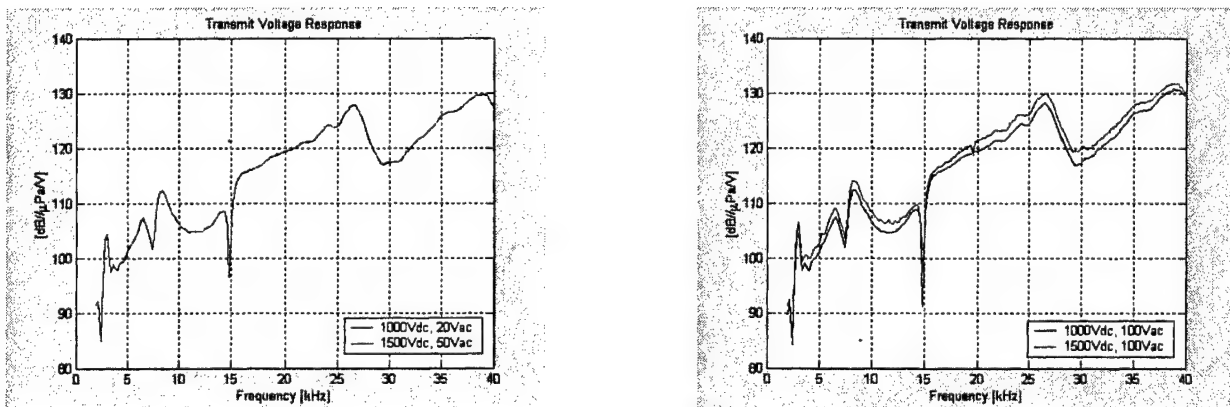


Figure 16: Transmitting Voltage Response for 0.040" aluminum flexing disk

3.4 Cube 1

The next EPAT sample received from MRL/PSU was the first example of the bulk cube configuration. Figure 17 is a picture of this item, designated "Cube 1". Note the multiple leads extending from the right side of the cube. There are two leads for each sheet within the stack, and this particular stack contains 23 sheets. General physical characteristics of the sample include a mass of 33.25 g, bulk density of 1721 kg/m³ (including all active layers, epoxy, and electrodes), and a bulk sound speed of 1328 m/s measured through one layer of the 23.

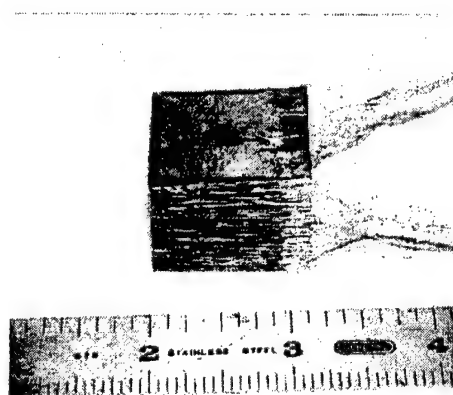


Figure 17: EPAT bulk mode Cube 1

3.4.1 Initial Tests, in Air

The first electrical tests on Cube 1 were done at very low levels to prevent inadvertent damage to the material. The bare cube was placed on a foam pad and all tests were performed in air. Test results for this configuration are shown in Figure 18. A weak resonance can be seen at 14.5 kHz.

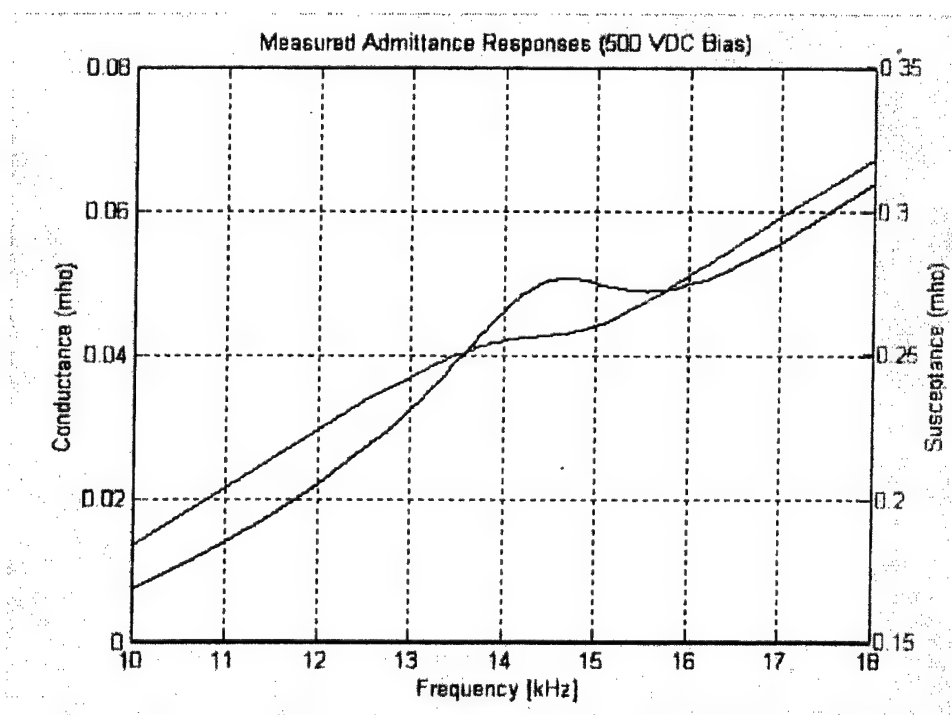


Figure 18: In-air tests on Cube 1 at 20 Vpp, 500 Vdc

3.4.2 In-water Tests

Since air tests showed a hint of a resonant condition, the cube was then assembled into the transducer test housing. Figure 19 shows the housing reconfiguration needed. The modifications included a thicker center section to fit the greater length of the cube. Once the transducer was assembled, it was tested (air-filled) on the bench. Figure 20 shows the admittance of the cube in the housing. For the plots shown, the drive voltage was 20 Vpp, and two different bias levels were used: 500 and 750 Vdc. The higher bias level does appear to show more activity through the region of interest, but characteristic resonant conditions are not seen, indicating the assembly is a lossy system and good efficiency should not be expected. In water test results showed very low output and efficiency.

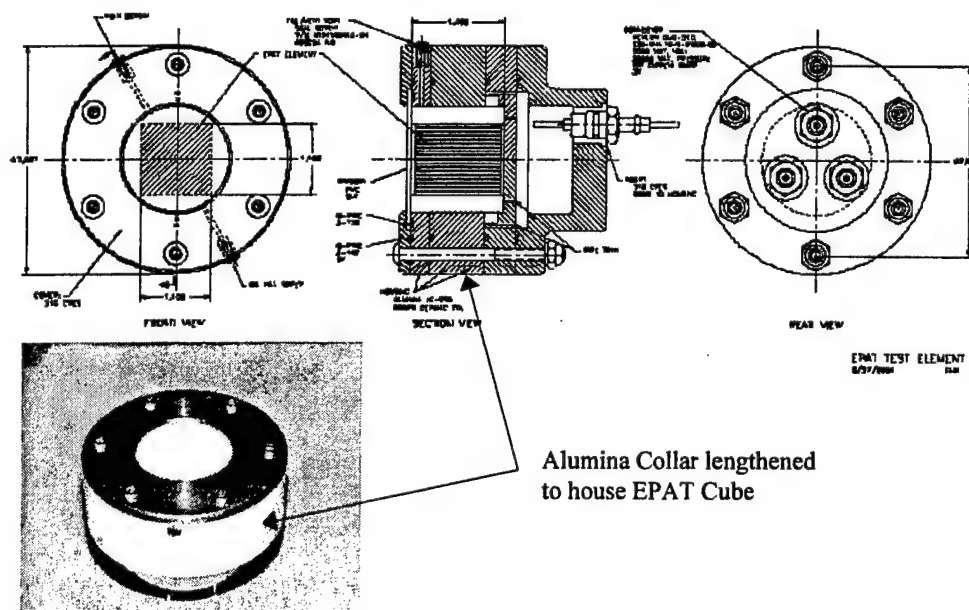


Figure 19: Cube 1 as assembled in test housing

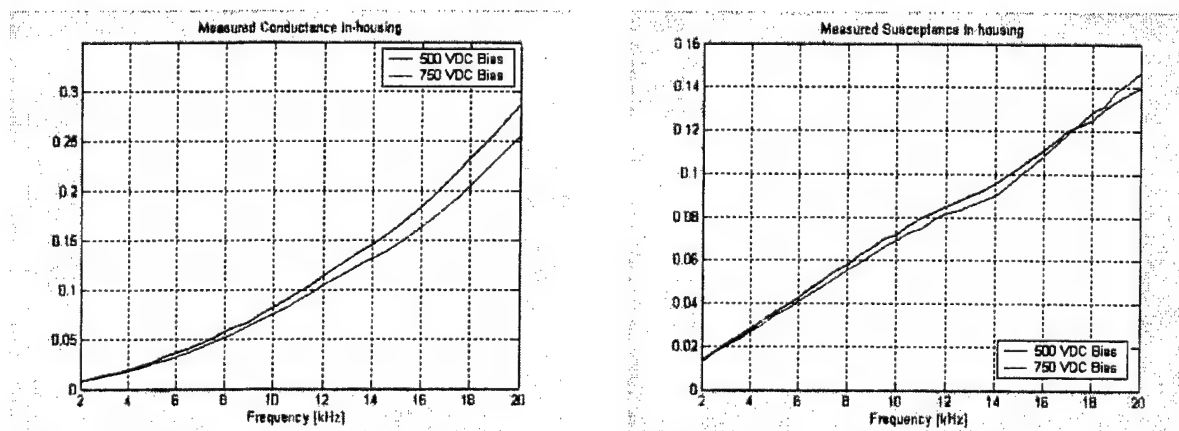


Figure 20: Admittance, Cube 1 in air, in test housing

3.5 Individual Plates

3.5.1 Construction

In July, 2002 Raytheon received another set of six plates from MRL/PSU. These samples were tested individually in air to determine material parameters, then assembled into a 31-mode test transducer designated Cube 2. Details of the six plates in this group are:

- Active material: stretched, irradiated, 68/32 P(VDF-TrFE) copolymer mix
- Each sheet consists of 30 layers, with each layer 30 μm thick
- 5 of the 6 plates contain 5 sheets or 150 layers; one plate contains 4 sheets
- The cube was made up of 4 of the 6 plates

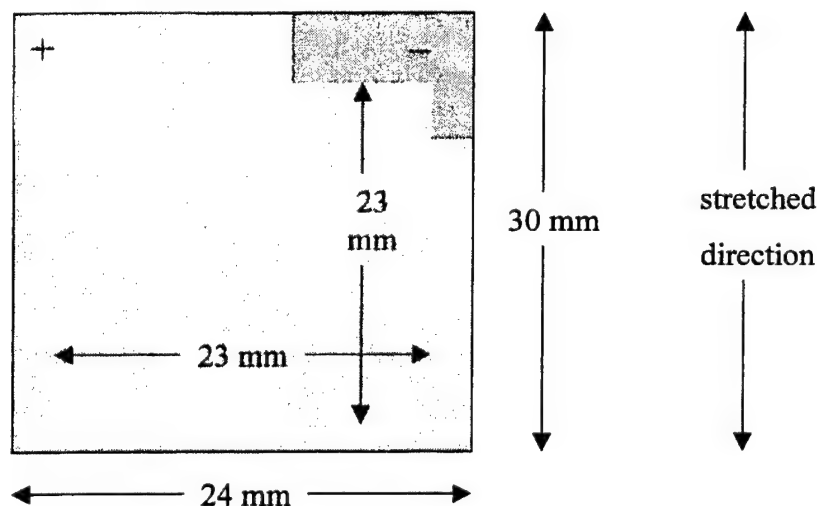


Figure 21: Plate electroding scheme

Each layer of material has 0.1 μm thick gold electrodes on both sides. The nominal size of the sheet and location of the electrodes is shown in Figure 21. Electrodes on opposite sides are reversed so the corner tab where the lead wire is attached is to the left on one side (as shown) and the right on the other. The energized area beneath the overlapping areas is $23 \times 23 = 530 \text{ mm}^2$. Including $\sim 1 \mu\text{m}$ thick glue lines, the electrode separation in the sheets is approximately 32 μm .

3.5.2 Electrical Tests on Plates, in Air

3.5.2.1 150-layer Plates

The electrical admittance of the plate was measured at low ac drive (10 Vrms) and varying dc bias. The plates were suspended in air by their leads for these tests. Typical admittance results are shown in Figure 22.

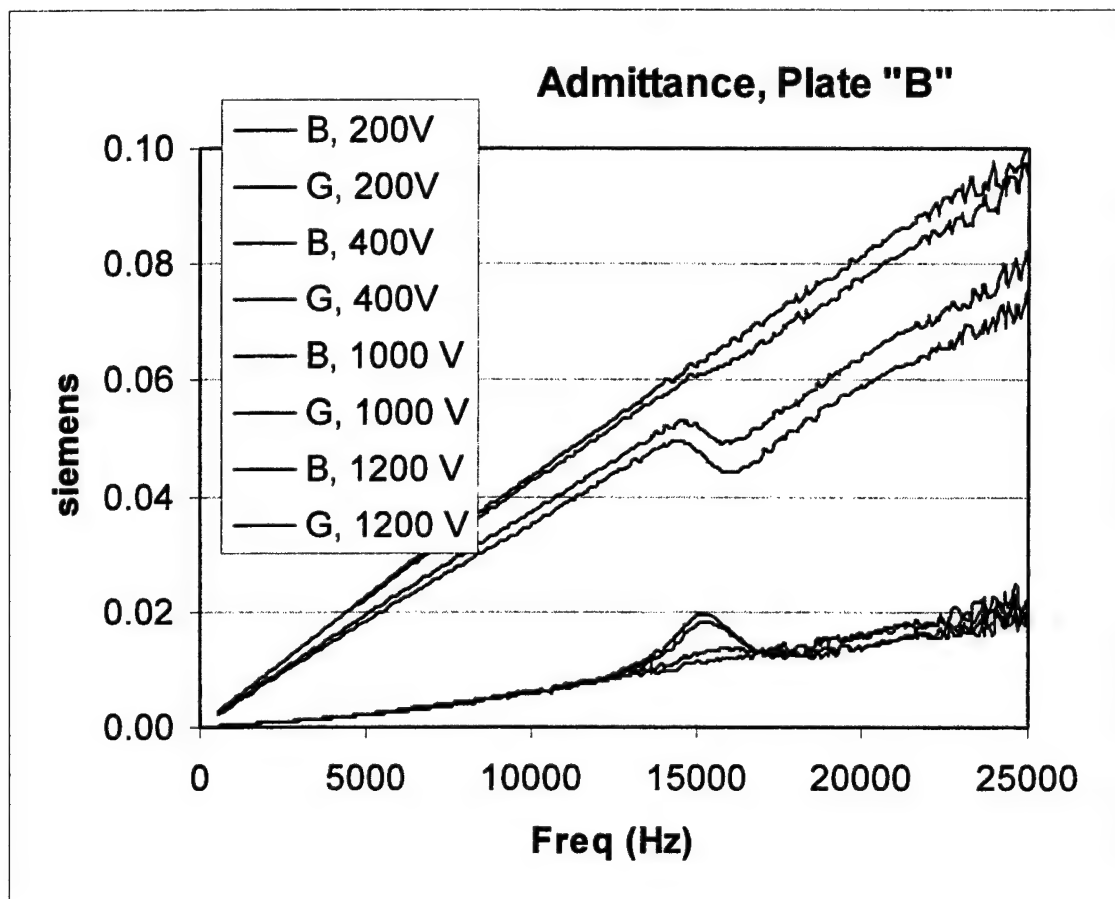


Figure 22: Plate admittance ($Y = G + jB$), in air

At low bias voltage both the conductance (G) and susceptance (B) curve rise smoothly, like a lossy capacitor. As the dc voltage increases signs of electrostrictive activity begin to appear, a dip in the B curve and a hump in the G curve. These results are analyzed by transforming them to capacitance ($C = B(\omega)/\omega$) and dissipation factor ($D = G(\omega)/B(\omega)$) curves, as given in Figure 23. In these plots the curves are labeled by dc bias *field* rather than voltage. Note that capacitance decreases with frequency and also with bias. The electrically-excited mechanical resonance is indicated by a dip in capacitance and a hump in dissipation near 15 kHz. The next pair of curves, Figure 24, is data for a different plate at higher bias levels, up to 50 MV/m, the electrical limit for this sample in air. Note how the resonant dip in the capacitance curve gets stronger as bias increases. On the dissipation curve the dashed line indicates the blocked (no motion) asymptote which is the same for all bias values. The blocked dissipation at resonance is the dielectric loss tangent, $\tan\delta$, which is rather high at 18% (typical $\tan\delta$ for piezoelectric ceramic is 0.5 – 2%).

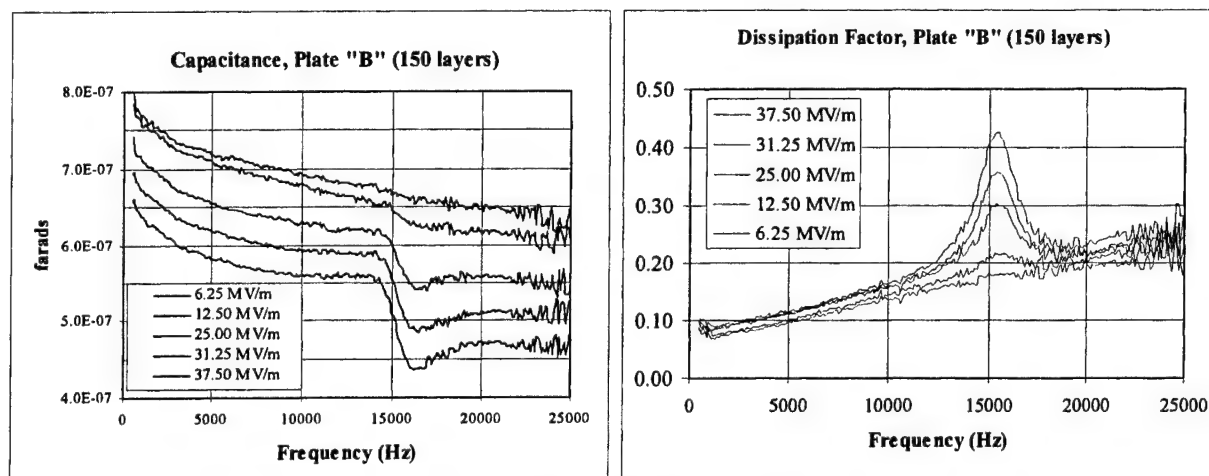


Figure 23: Curves derived from admittance for Plate "B"

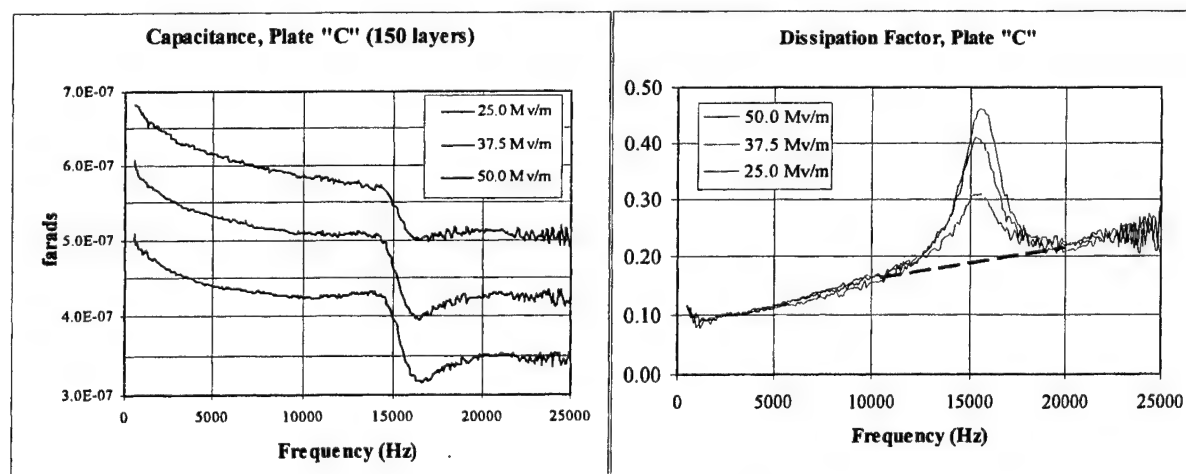


Figure 24: Plate "C" data at higher bias fields

In-air tests on this group of plates were repeated at varying bias levels up to 1200 Vdc (37.5 MV/m) for most samples, and up to 50 MV/m on Plate "C". Because of the high $\tan\delta$ losses a special data reduction technique was used to extract material properties from admittance data¹.

Material properties at a given bias voltage were similar from plate to plate. Results for Plate "C", which experienced the highest bias, are given in Figure 25. Parameter M in the table in Figure 25 is another term commonly called "Figure of Merit", this one given by $Q_m k^2 / (1 - k^2)$, where k is the effective coupling (which is different from k_{31}).

Bias, Vdc	MV/m dc	M	Q_m	k_{31}	K_3^T	f_r (kHz)
800	25	0.130	7.7	0.143	24.7	15.3
1200	37.5	0.238	6.7	0.206	20.8	15.3
1600	50	0.301	6.1	0.241	17.2	15.2

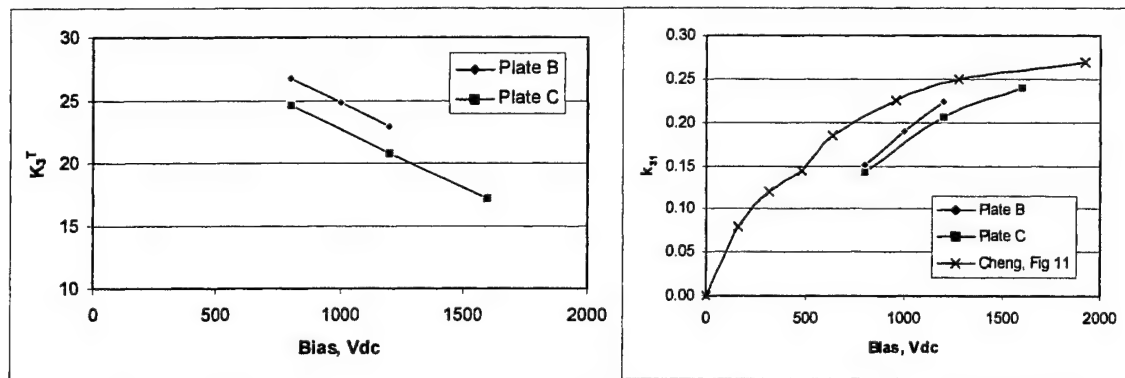


Figure 25: Data summary for Plate "C" in air, 10 Vrms excitation

Dielectric constant, K_3^T , decreases linearly with bias, and coupling coefficient, k_{31} , increases with bias, but not quite to the values measured² on single sheets at MRL/PSU. This loss of coupling is thought to be due to the inactive compliance of the unelectroded border surrounding the active area (see Figure 21). Resonant frequency and Q_m do not change appreciably with bias level.

3.5.2.2 Thin Sheets

Because electrical breakdown occurred regularly at the higher bias levels, MRL/PSU made some modifications to their fabrication process and produced two sets of thinner (50-layer) sheets which could be tested to higher bias fields if immersed in dielectric fluid to suppress surface arc-over. The same samples were later tested at elevated temperatures. The thin sheet tests actually took place after the Cube 2 tests, but are reported in this section for report continuity.

The first group of thin sheets, designated S1, S3, B3, S4 and S7, were received in January and February, 2003. The bias levels in these tests started at the highest level of the earlier tests, 50 MV/m, and went up to 85 MV/m. Two resonances were seen for every sample: a lower one (13.5 to 15 kHz) which was assumed to be the 31 length mode resonance, and a higher one (24 to 27 kHz) which was assumed to be the 32 lateral mode. Only the lower frequency resonances were studied because that mode corresponds to mechanical output along the enhanced (stretched) axis of the material.

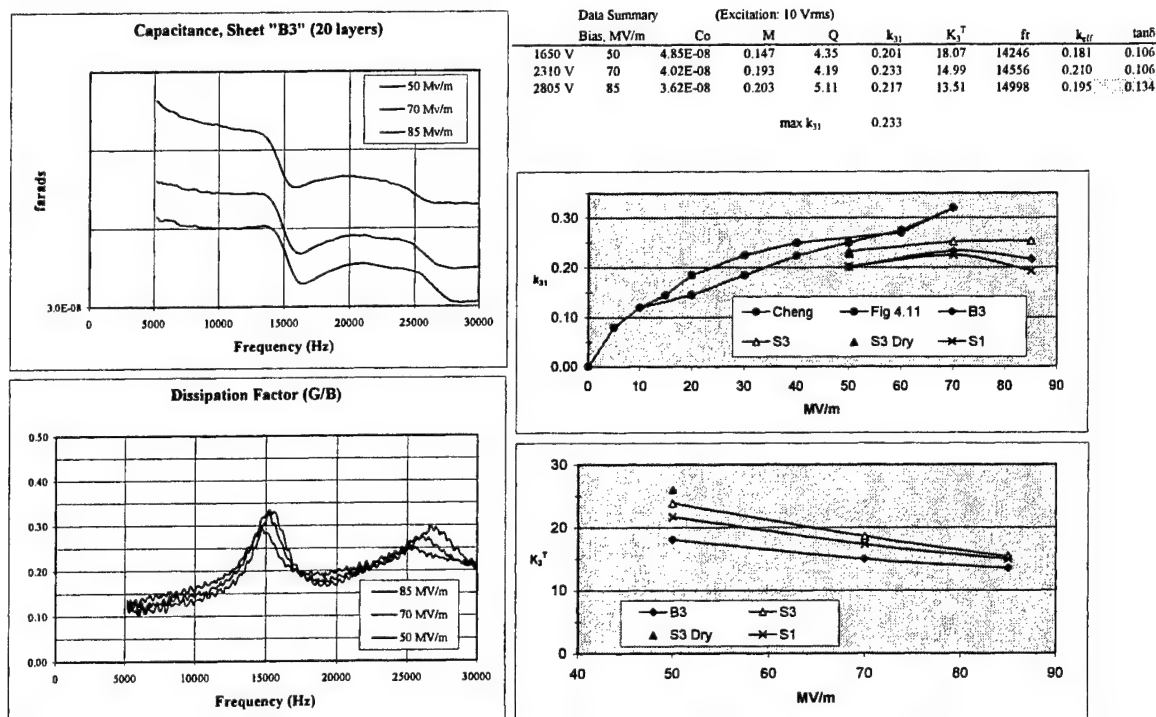


Figure 26: Data summary for thin sheets at room temperature

Room temperature results for thin sheets S1, S3 and B3 are given in Figure 26. The two graphs on the left and the table in this figure are for sheet B3; the other two samples were similar. Tests on sheet S3 at 50 MV/m, with and without Fluorinert Liquid FC-77 (contrast the open and closed green triangle data points), demonstrated that a shallow layer of liquid did not markedly affect the electromechanical activity. Increasing the bias beyond 50 MV/m caused further decrease in dielectric constant, and inconsistent change in coupling coefficient. This was disappointing because a steady increase in coupling with bias was the desired result. The "Fig 4.11" curve on the coupling graph was taken from a MRL/PSU thesis (author unknown). One positive finding on these tests was a lower $\tan \delta$, indicating that the refined fabrication methods did result in lower dielectric losses.

Figure 27 shows the effect of elevated temperature for one sheet, S4. The first observation is that the resonance frequency decreased significantly, from around 14.5 kHz at room temperature to around 10.5 kHz at the higher temperature. Since it is unlikely the density changed, one concludes that the 31 modulus decreased by 50% when heated to 40°C. The second observation is that the dielectric constant increased considerably (+80%) when heated, basically restoring the dielectric decrease accompanying high bias. Perhaps the most encouraging aspect of heating (although this is difficult to see in Figure 27) is the large decrease in $\tan \delta$; at 85 MV/m this parameter dropped from 0.145 to 0.033. This is an important result because it means a transducer made of EPAT material would reach thermal equilibrium instead of melting due to thermal runaway. Coupling and Q_m did not change appreciably with temperature.

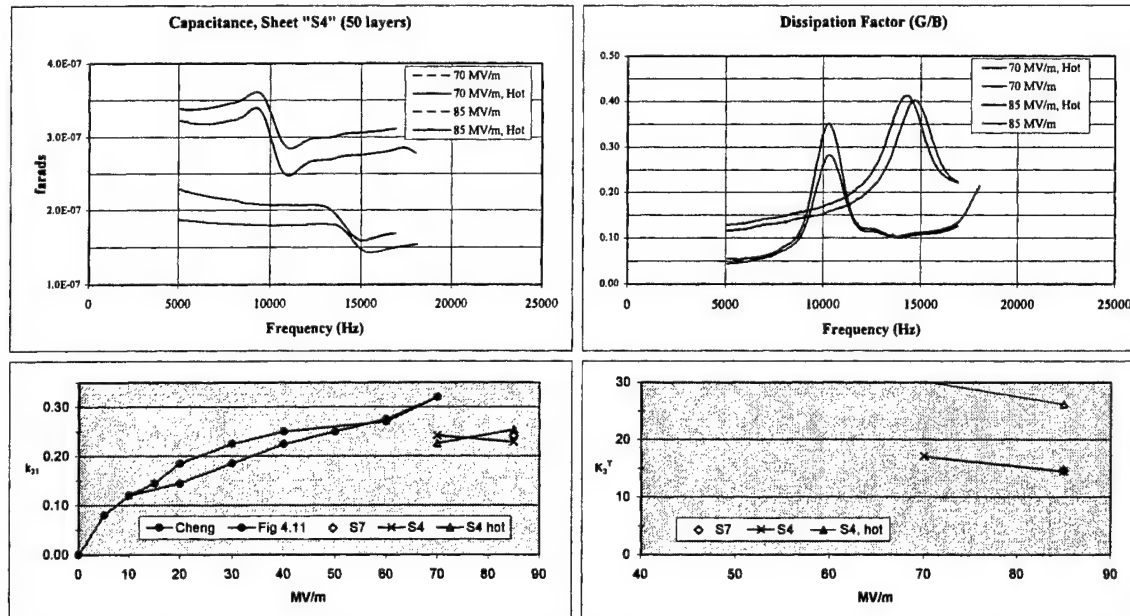


Figure 27: Thin sheet S4 at room temperature (plain) and 40°C ("Hot")

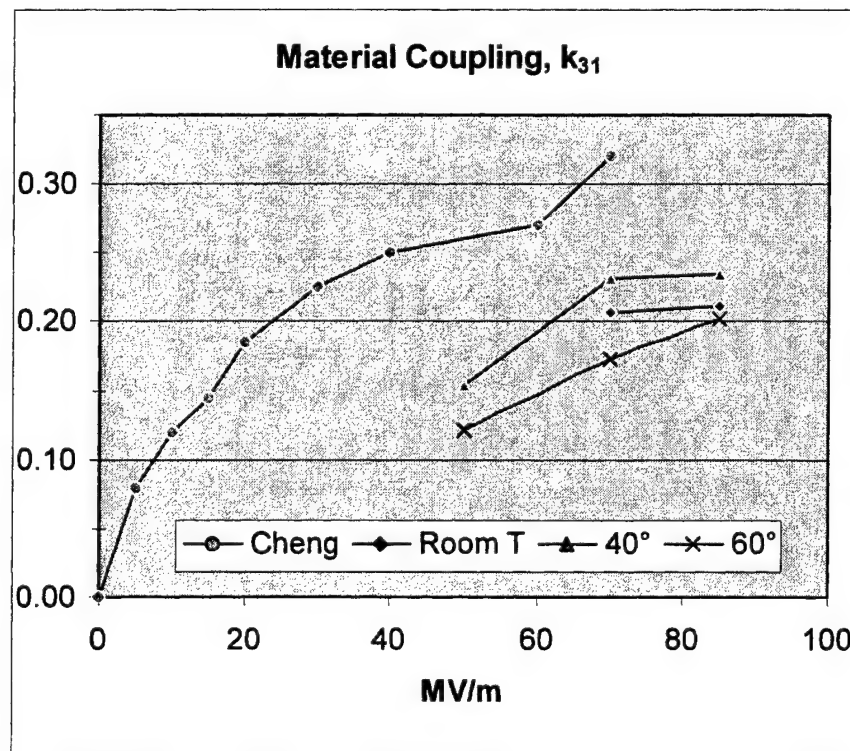


Figure 28: Coupling vs temperature and bias for Sheet S8

Later a second pair of thin sheets, S8 and S9, were received and tested. Sheet S9 failed due to electrical breakdown when biased to 70 MV/m at room temperature. Sheet S8 survived biasing and was tested at three temperatures (24°, 40°, 60°C) and three bias fields (50, 70, 85 MV/m) with the following results.

- Coupling increased with bias at all temperatures
- Coupling was higher at 40°C than at either 24° or 60°
- Dielectric constant increased significantly with temperature, but decreased with bias
- Tan δ decreased significantly with temperature, and was not very sensitive to bias

Coupling curves for this case are shown in Figure 28. The overall conclusion of the thin sheet tests is that performance of EPAT material improves with temperature, with optimum coupling occurring around 40°C.

3.6 Cube 2

3.6.1 In-water Tests, Housing Filled with Gas

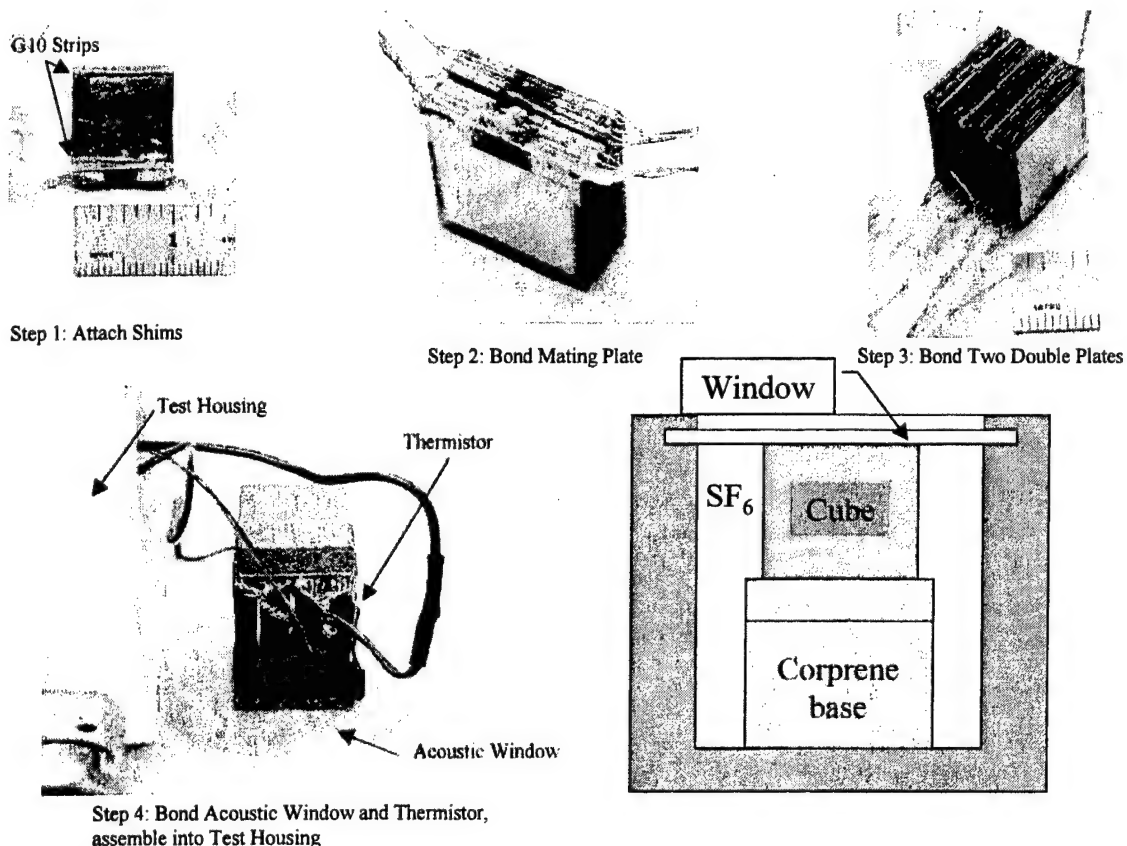


Figure 29: Stages of Cube 2 transducer assembly

Four sets of sheets were separated using thin strips of G-10 fiberglass and assembled into a cube as shown in Figure 29. After assembly the housing was filled with SF₆ gas at 1 atm.

High bias levels were not attempted with Cube 2 because the transducer was gas filled and prone to electrical breakdown, consequently the acoustic results shown in Figure 30 are not impressive. Electrical conditions for this test were 25 MV/m bias and 40 Vrms drive signal. The resonance was a bit lower than the individual plate resonances due to water loading, and the TVR curve peak was quite broad ($Q=3.3$) indicating a heavily damped resonator. The strong damping results in a fairly flat receiving response (barely detectable resonance). The receiving sensitivity for Cube 2 over the range 5 to 25 kHz was $-178 \pm 1 \text{ dB re V}/\mu\text{Pa}$.

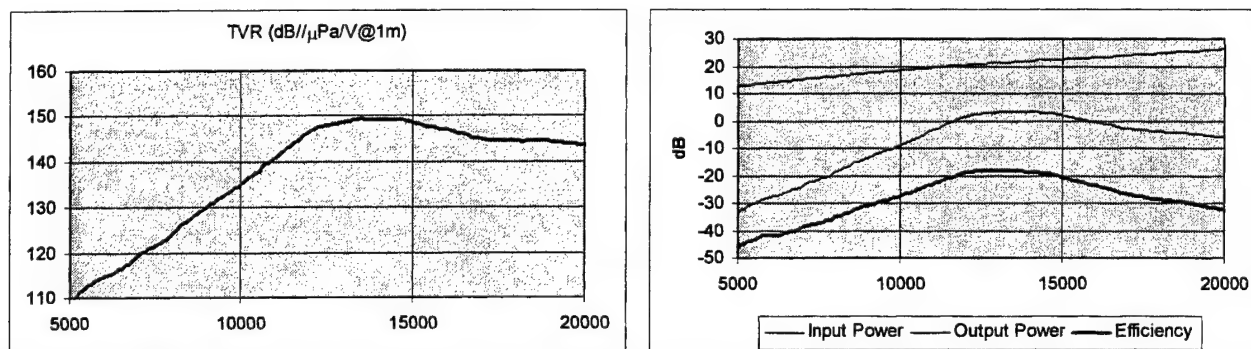


Figure 30: Cube 2 acoustic data (gas filled, 25 MV/m bias, 40 Vrms drive)

The directivity of the projector was measured in order to calculate electro-acoustic efficiency. Figure 31 shows two beam patterns taken at 14.2 kHz. The DI at the 13.5 kHz resonance was calculated to be 7.4 dB resulting in a peak efficiency of 1.6%. Scaling directivity with frequency one obtains the curves of input and output power and efficiency shown on the right in Figure 30.

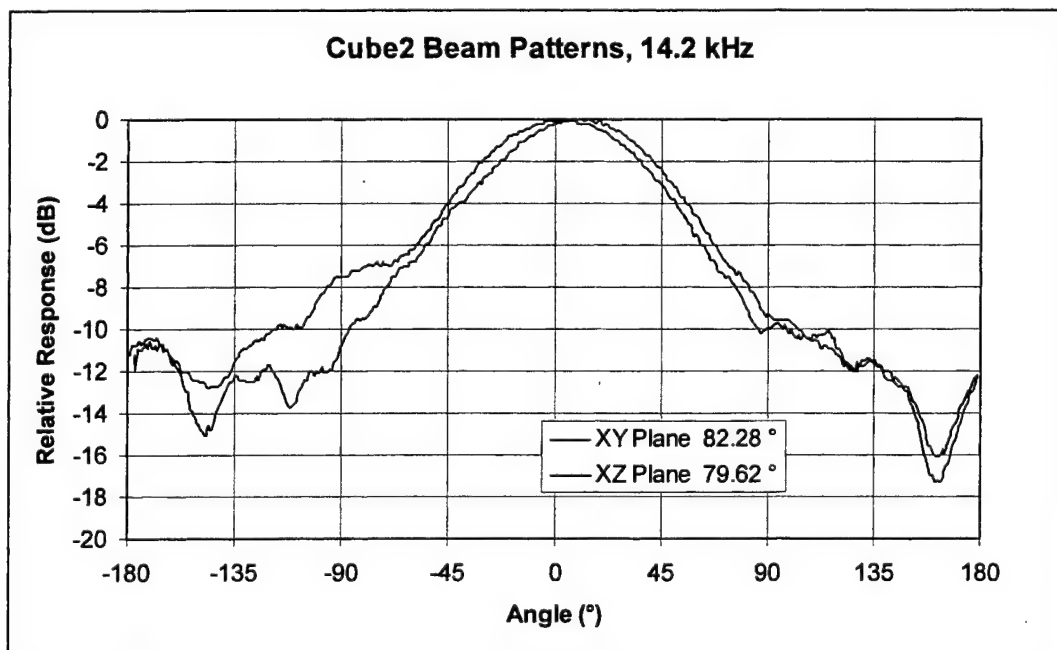


Figure 31: Vertical and horizontal beam patterns

Some increase in efficiency can be expected at higher bias. Starting from the results above and using the variation in k_{31} and K_3^T with bias measured on Plate C, and further assuming Q_m does not change with bias, we calculate that Cube 2 efficiency would increase to 3.1% at 50 MV/m.

If these very low efficiency values persisted at higher temperatures it would restrict usage to very low duty cycles. Thermal analysis of the cube showed that 1.3 W of continuous input heat power would produce a temperature rise of 40°C at the center of the cube, and this was taken as the upper limit on acceptable heating. Extrapolating Cube 2 data to higher drive levels, it was decided that drive voltages above 40 Vrms at 1% duty cycle would exceed this heating limit. Later in the program it was discovered that the dielectric loss part of the inefficiency *decreases* with temperature, so restricting drive levels to prevent thermal runaway may not be necessary. In light of these results it is recommended that the subject of losses and efficiency be given a thorough review at the beginning of any future EPAT transducer study.

3.6.2 In-water Tests, Housing Filled with Fluorinert Liquid

To permit testing at higher voltages (both bias and drive) the test housing was filled with Fluorinert FC-77 dielectric liquid. Two other changes were made at this time: the rear of the cube was attached to a quarter-wavelength lead tail mass and that was fastened to a thin sheet of Corprene, and the front face was detached from and positioned 5 mm behind the acoustic window (see Figure 32).

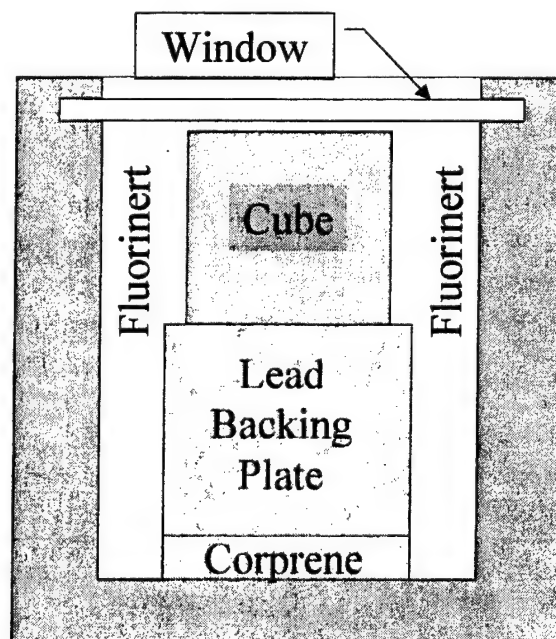


Figure 32: Cube 2 in fluid-filled housing configuration

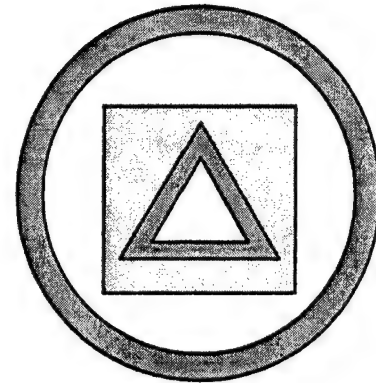
Electrical arc-over was experienced during initial air tests of the fluid-filled configuration. One successful frequency sweep was made at 25 MV/m bias, but loud pops were heard during the 50 MV/m run. When the bias was removed electrical checks showed decreased capacitance and

increased dissipation, typical signs of an arc-over. The unit was disassembled, one low impedance plate was taken out of the circuit, and it was then refilled with liquid. A repeat of the 25 MV/m sweep was successful, but a loud snap and bright flash occurred during the 50 MV/m run. Post mortem investigation revealed two bad plates in the cube, and the test was stopped.

3.7 Tripod Conceptual Design

After Cube 2 failed a series of 50-layer plates were made and tested. The object of these tests, reported in Section 3.5.2.2, was to evaluate process changes made to increase breakdown strength and to investigate material parameter changes at higher temperatures.

After discovering that material performance generally improved at elevated temperatures, there was a desire to build and test another transducer, but the quantity of 1.1 mm thick plates on hand was not great enough to assemble a 3rd cube. Consideration was then given to building a new transducer driver assembly by arranging three such plates into a triangular truss, fastening one end to a tail mass, and covering the opposite end with a thin rigid plate to create the radiating face. This concept is shown in the sketch above in which the outer ring depicts the test housing wall and the gray square the tail mass. To permit use of higher bias fields this driver was to be fluid filled, small gaps would be placed at the corners of the triangle to allow flooding of the interior, and the interior space would also be lined with pressure relief material. The semi-rigid acoustic window would be replaced with a flexible membrane to allow for hydrostatic compensation. Due to time constraints this driver never reached the test stage.



To review the transducer design concepts considered on the project, the most desirable 31-mode configuration was deemed to be the spiral wrap described in Section 2.2, but building one of these required production of EPAT material shaped in a long ribbon, a goal not yet attained. The alternate configuration involved stacking a series of plates into a cube. Two examples of this type were built and tested. A third concept, which would require far fewer plates than the cube, consisted of arranging three plates into a triangle, but an example of this concept was not completed in time.

4.0 SUMMARY OF PROGRAM RESULTS

Stretched and irradiated copolymers of PVDF have promise as the active material in low-cost acoustic projectors based on a combination of favorable properties.

- Very high electrically-induced elastic strains ($\sim 0.4\%$)
- Good electrode adhesion, even at such high strains
- Favorable elastic properties (good pc match to water)
- Ruggedness (no shock or overstress concerns)
- Acceptable transverse mode coupling factor
- Low material cost

Expected k_{31} coupling has yet to be realized in material samples tailored for transducer use, but there is no reason to doubt that the values observed on laboratory samples (~ 0.27) will not be obtained in the favored spiral wrap projector configuration. Low material cost is expected based on the low cost of raw material and future high production volumes, however methods for lowering the cost of stretching and irradiation have not been demonstrated.

The benefits listed above must be balanced against a few drawbacks. Foremost of these is that the material does not exhibit useful electromechanical activity unless biased with a fairly high electrical field (30 to 50 MV/m dc). Applying a combination of dc bias voltage and ac driving signal complicates the driving electronics, and achieving such high fields with standard film thickness requires high voltages which in turn requires greater corona suppression measures and impacts cabling and connectors. Furthermore, experimental samples received so far have been prone to electrical breakdown at high fields unless bathed in insulating fluid. However process improvements at MRL/PSU resulted in samples having higher breakdown strength, and more progress in this area is expected.

The material has very high dielectric loss ($\tan\delta$) at room temperature, and this implies very low electromechanical efficiency. However $\tan\delta$ drops to reasonable levels at elevated temperatures, and the material should reach thermal equilibrium when used at typical duty cycles. The changing elastic and electrostrictive properties during the warm-up period would result in shifting resonance frequency and output levels until stabilized. Coupling does not change substantially with temperature.

In summary, electrostrictive polymers may offer a new way to make conformal arrays for future sonar applications. Polymer arrays could be very low cost compared to technologies in use today. Raytheon's EPAT program demonstrated the first projectors utilizing electrostrictive polymer material, but these early examples did not fully achieve the acoustic performance anticipated. Electrostrictive polymer production needs to be optimized. It is our belief that PVDF terpolymers may offer high volumes of even lower cost material which will fully realize the performance potential of polymer materials. We look forward to designing and optimizing terpolymer sonar projectors in the future.

5.0 REFERENCES

¹ W. J. Marshall and G. A. Brigham, "Determining equivalent circuit parameters for Low Figure of Merit transducers", submitted to Acoustic Research Letters Online – ARLO (in review).

² Z.-Y. Cheng, "Electrostrictive poly(vinylidene fluoride-trifluoroethylene) copolymers", Sensors & Actuators A 90 (2001), 138-147.

APPENDIX 1 A

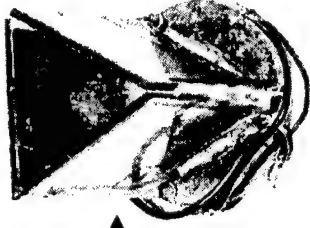
Summary of Measurements on EPAT Tripod Transducer

Bill Marshall
Raytheon IDS
Portsmouth RI

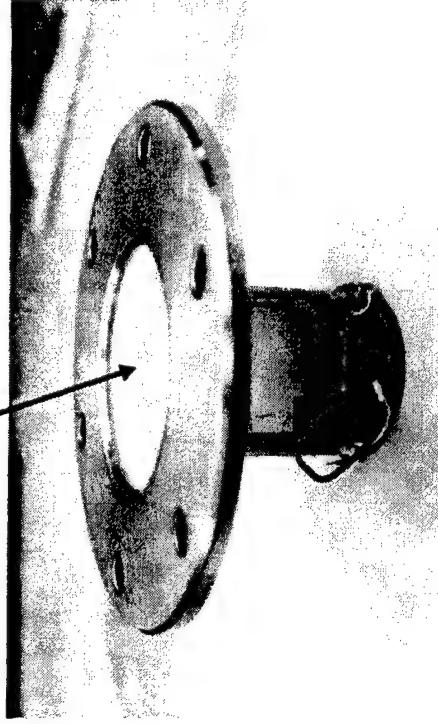
June 1, 2004

Configuration of Test Unit

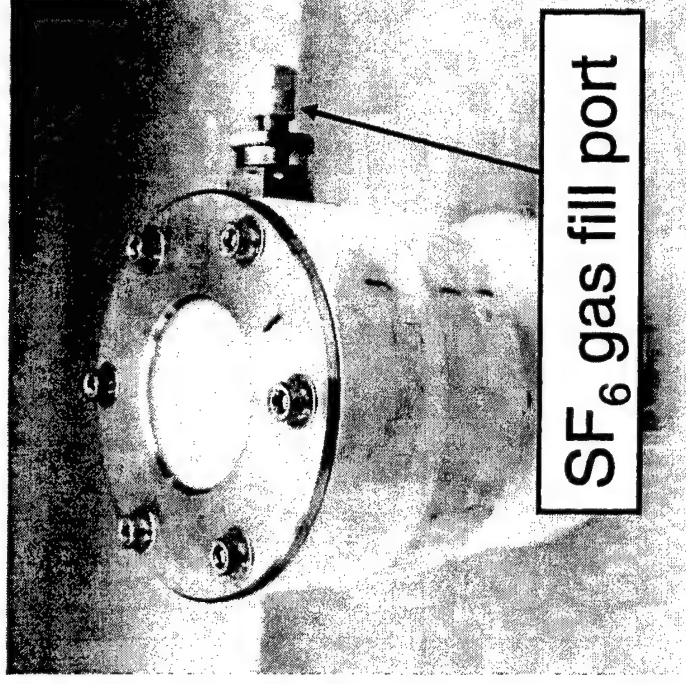
Triangular truss of
EPAT sheets on
Corprene base



Driver bonded to
Urethane window



Final assembly



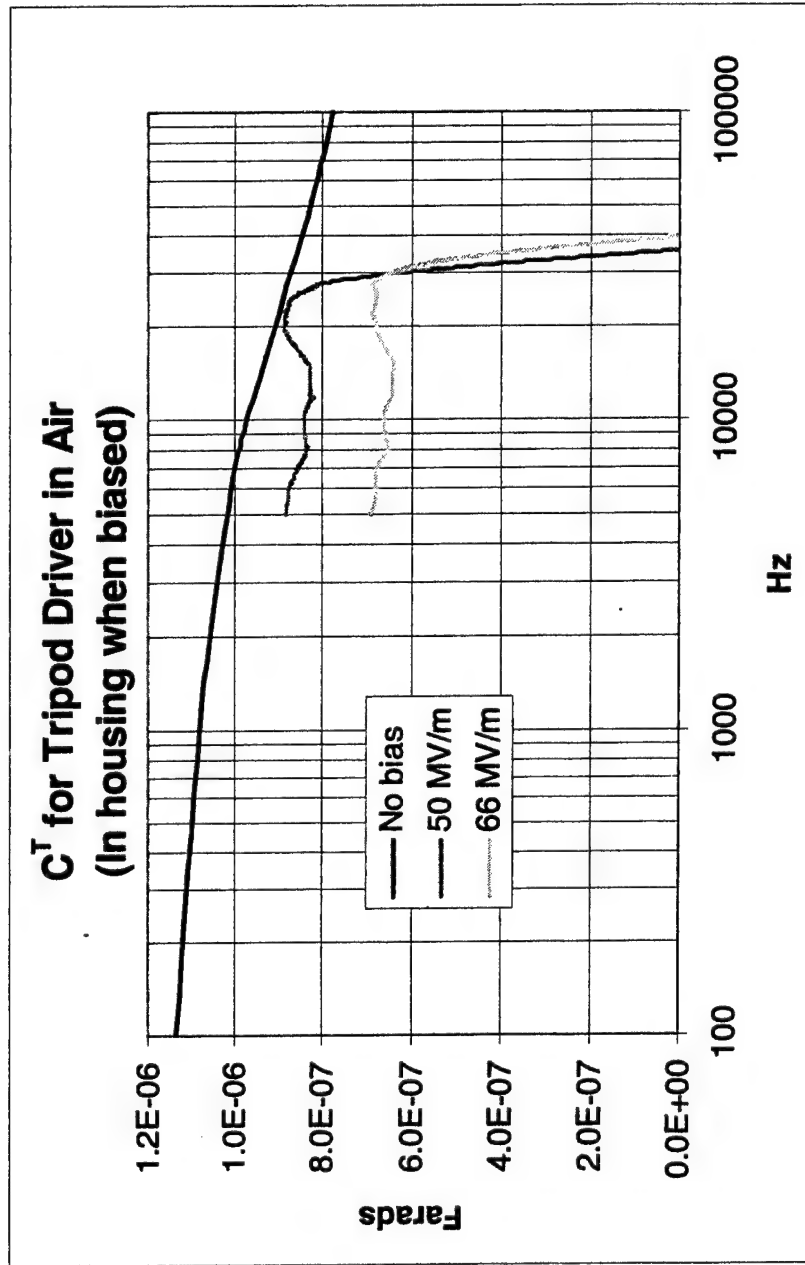
SF₆ gas fill port

Analysis of In-Air Admittance

- Free (unblocked) dielectric constant K_3^T [page 4]
 - Decreases smoothly with frequency when unbiased
 - Decreases further, and shows signs of electromechanical activity, when electrically biased
- At maximum tested bias field (66 MV/m)
 - Single mechanical resonance: 40 kHz [pages 5, 7]
 - Mechanical Q is low: 1.9
 - Coupling factor is extremely high: 0.88
- Conclusion: Experimental error or material properties drifting throughout test, because
 - Material coupling k_{31} is 0.21 at this bias field *
 - Device coupling cannot be greater than material coupling

* Raytheon: Electrostrictive Polymer Acoustic Transducer (EPAT) Final Report (Sept. 30, 2003), Fig. 28

Free Capacitance at 3 Bias Levels



Variation of free dielectric constant with bias field, at 10 kHz

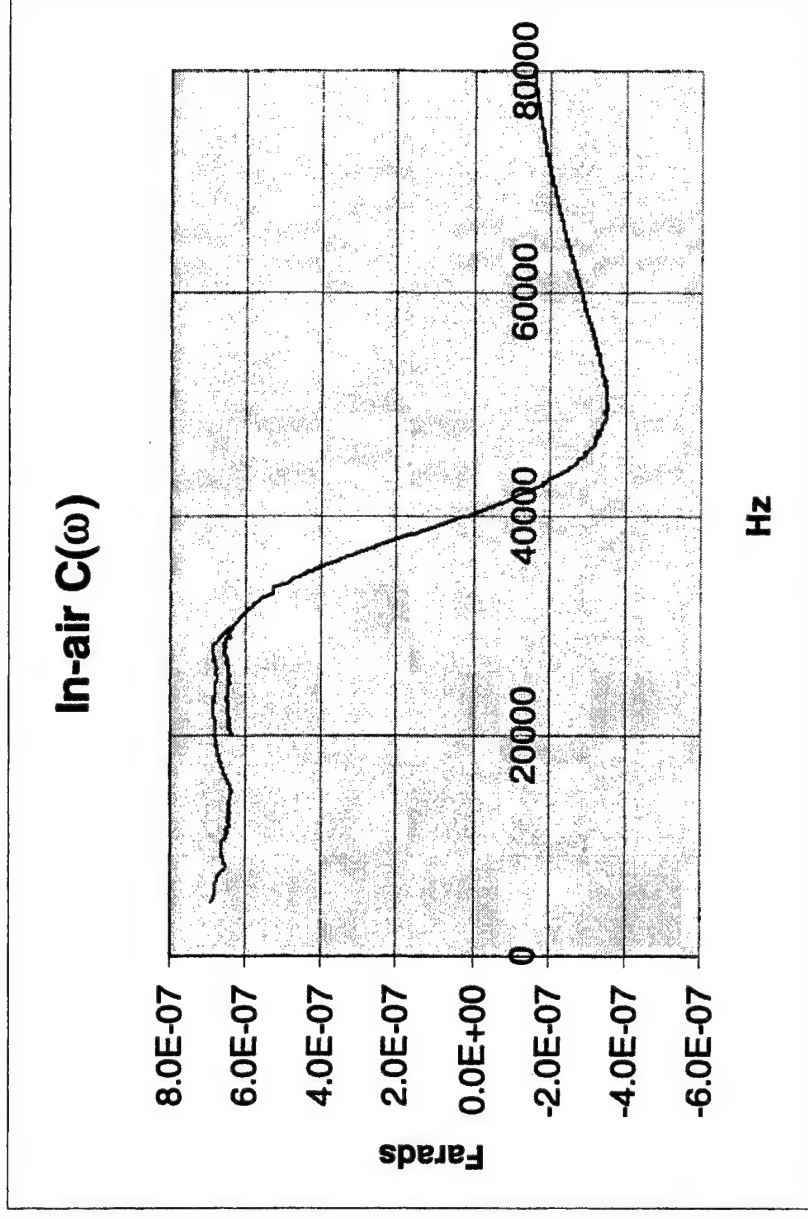
Bias, MV/m	C ^T (μF)	K ₃ ^T
0	0.975	30
50	0.844	26
66	0.663	20

Analysis of In-Air Admittance for 66 MV/m Bias Field

Raytheon
Integrated Defense Systems

- Using low-M
analysis method *

- $f_r = 40.2 \text{ kHz}$
- $C_0 = 0.151 \text{ uF}$
($K_3^S = 4.67$)
- $Q_m = 1.92$
- $K_{\text{eff}} = 0.88$



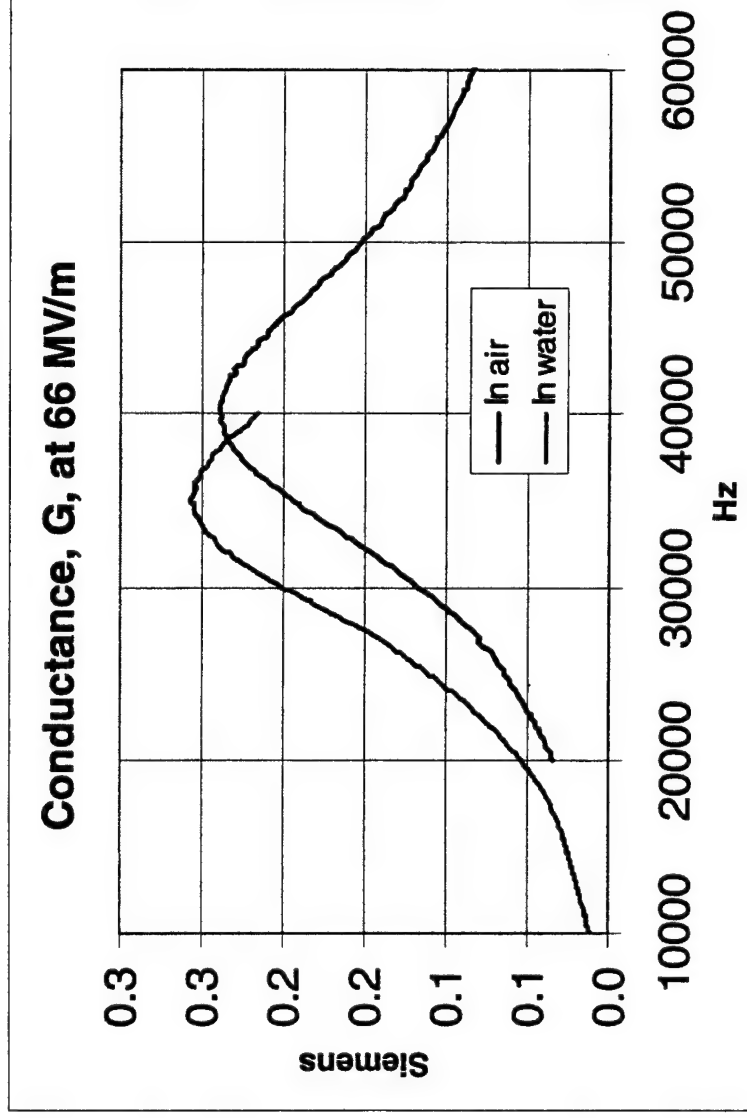
* Marshall et al., Acoustic Research Letters Online 5 (3), 106-110 (July 2004)

Transmitting Performance at 66 MV/m Bias Field

- In-Water Conductance [Page 7]
 - Single isolated resonance at 35 kHz
 - Similarity of air & water G indicates low efficiency
 - No signs of activity at 15 kHz (lateral resonance of sheet)
- Transmitting Voltage Response (TVR) [Page 8]
 - Weak peak at 15 kHz (lowest longitudinal mode of sheet)
 - Sharp dip at 28 kHz
 - Broad peaks at 24 and 31 kHz
- Beam Pattern at 35 kHz [not shown]
 - 87° beam width (consistent with 1.3" dia. piston radiator)
 - DI = 6.9 dB
- Electroacoustic Efficiency: $\eta_{ea} = 0.0010$ (-30 dB)
 - Cube of same material had higher efficiency (-18 dB) at lower frequency and lower bias *

* Raytheon: EPAT Final Report (Sept. 30, 2003), Fig. 30

In-Water Conductance



Since maximum G is larger in water than in air, standard efficiency formula yields $\eta_{ea} > 1$

Results of acoustic measurement:
 $\eta_{ea} = 0.001$ at 35 kHz

On-Axis TVR, 66 MV/m Bias Field

Raytheon

Systems Company

Thu Apr 22 8:56:40 2004

XRI4L040422_084601

Transmit Voltage Response

Transmit Response

EPAT

EPAT TRIPOD 1.3kVdc 20Vac (2A max)

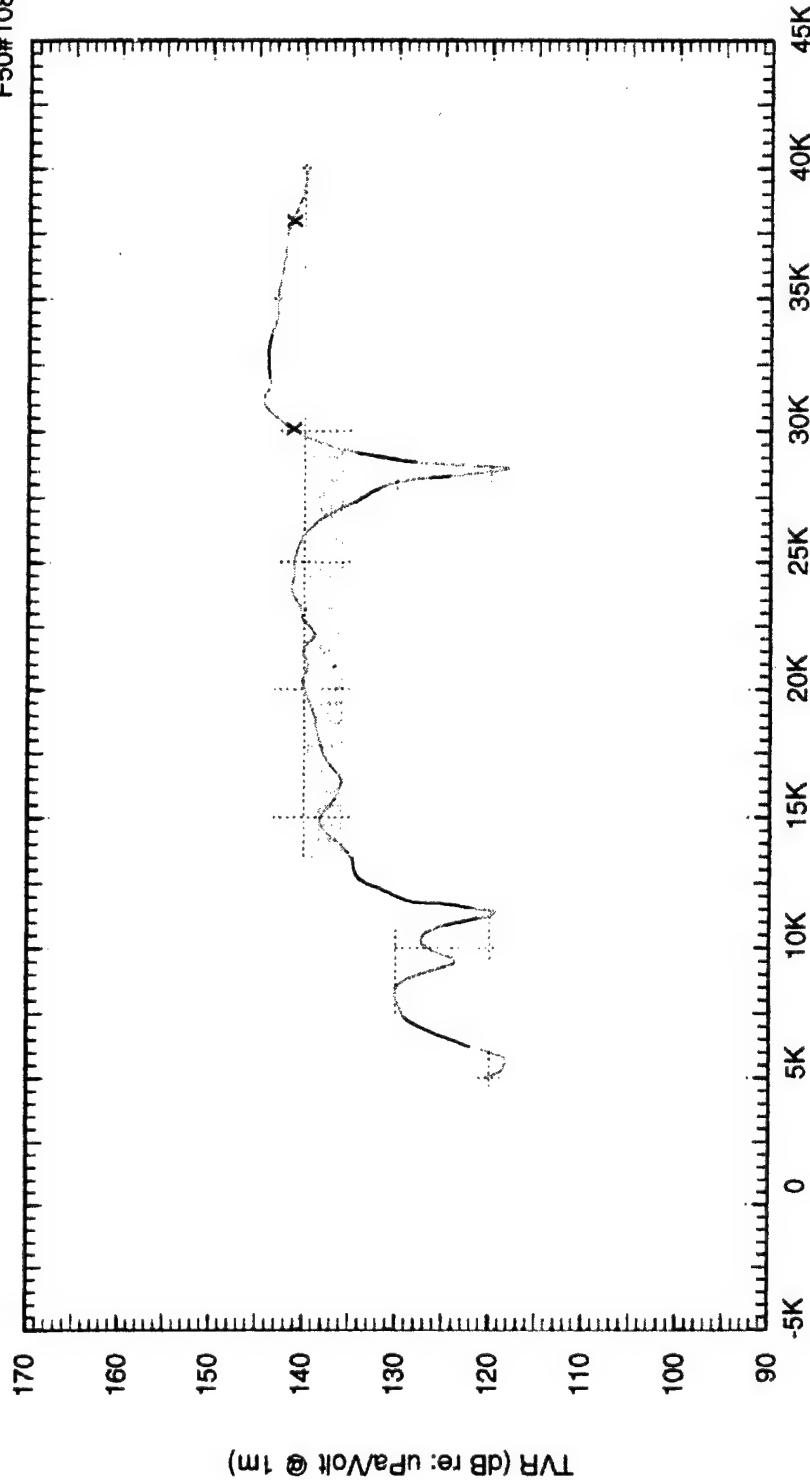
WATER

19.44 deg C

3.53 kPa(2.49 m)

3.66 m

F50#108.RVR



Peak Response: 144.38 at 31.2KHz f1: 30.078KHz f2: 37.959KHz BW: 7.8808KHz Q: 3.959

Unclassified

Overall Summary of the Work

- The Tripod transducer was made from leftover sheets of copolymer material remaining at the conclusion of previous experiments on cubes.
- The main acoustic resonance for the 3-sheet assembly, in its housing, was considerably higher than for cubes in the same sheet size and in the same housing. We conclude that the resonance is dominated by the stiffness of the acoustic window, not the active material, hence the higher frequency and lower efficiency.
- The relatively thick acoustic window was a leftover used for expediency, but a rugged window is necessary to prevent buckling of the thin sheets under hydrostatic pressure.
- The driver assembly survived testing up to 66 MV/m dc, but with some sample deterioration (peeling electrodes, lower capacitance).
- The anomalous admittance result (high K_{eff}) may be due to material properties varying during the test, perhaps as a result of sample heating or electrode erosion. There was insufficient time to confirm this hypothesis with further testing.
- The measured beam width relates to an ideal piston radiator of 1.3" diameter, consistent with the actual window diameter of 1.66".

APPENDIX 1 B



US006423412B1

(12) **United States Patent**
Zhang et al.

(10) **Patent No.:** **US 6,423,412 B1**
(45) **Date of Patent:** **Jul. 23, 2002**

(54) **FERROELECTRIC RELAXER POLYMERS**

(75) **Inventors:** **Qiming Zhang; Vivek Bharti**, both of
State College, PA (US)

(73) **Assignee:** **The Penn State Research Foundation**,
University Park, PA (US)

(*) **Notice:** Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 0 days.

(21) **Appl. No.:** **09/195,061**

(22) **Filed:** **Nov. 18, 1998**

Related U.S. Application Data

(60) Provisional application No. 60/065,641, filed on Nov. 18,
1997, and provisional application No. 60/093,718, filed on
Jul. 22, 1998.

(51) **Int. Cl.⁷** **B32B 27/30; G01N 27/00;**
H01H 57/00

(52) **U.S. Cl.** **428/421; 428/910; 422/82.01;**
200/181; 522/156

(58) **Field of Search** **422/82.01; 200/181;**
428/421, 910; 522/156

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,635,812 A * 6/1997 Eschbach et al. 320/1
5,679,753 A * 10/1997 Ohigashi et al. 526/255

OTHER PUBLICATIONS

Ferroelectrics, 1990, vol. 109, pp. 303–308, F. Macchi et al.
“Effect of Electron Irradiation on the Ferroelectric Transi-
tion of P (VDF–TrFE) Copolymers” No Month.

Macromolecules 1985, vol. 18, pp. 910–918, Andrew J.
Loving, “Polymorphic Transformations in Ferroelectric
Copolymers of Vinylidene Fluoride Induced by Electron
Irradiation” No Month.

Nuclear Instruments and Methods in Physics Research, B46
(1990), pp. 334–337, F. Macchi et al., “Micromechanical
Properties of Electron Irradiated PVDF–TrFE Copolymers”
No Month.

* cited by examiner

Primary Examiner—Paul Thibodeau

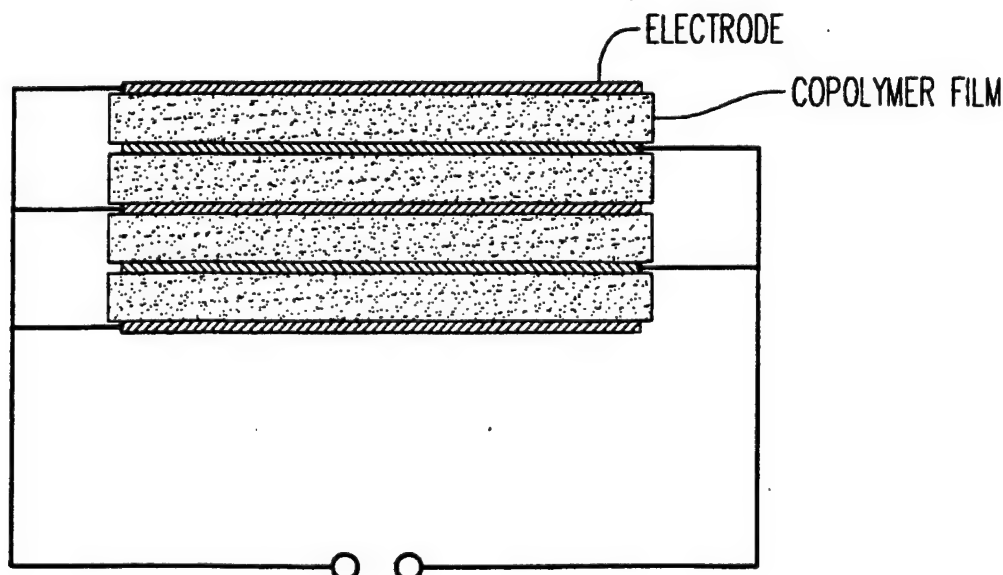
Assistant Examiner—Ramsey Zacharia

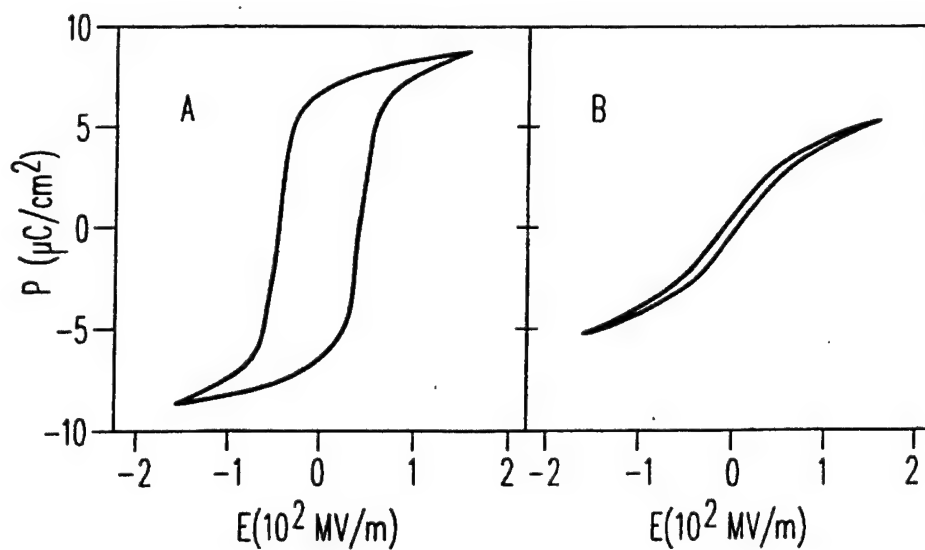
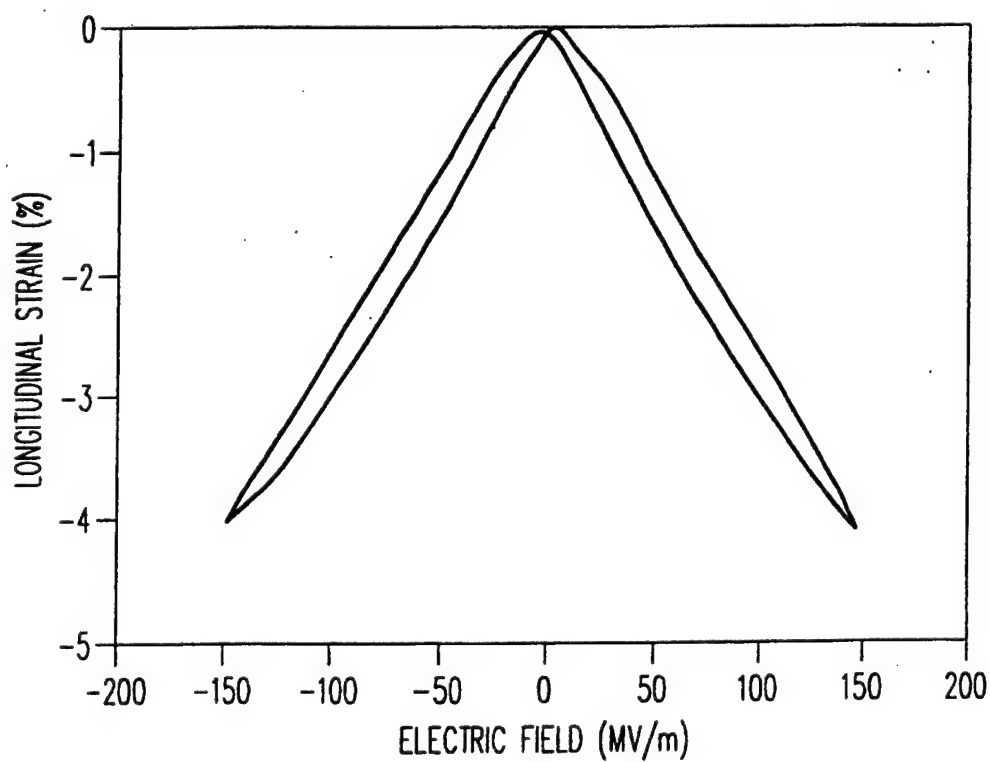
(74) *Attorney, Agent, or Firm*—Ohlandt, Greeley, Ruggiero
& Perle, L.L.P.

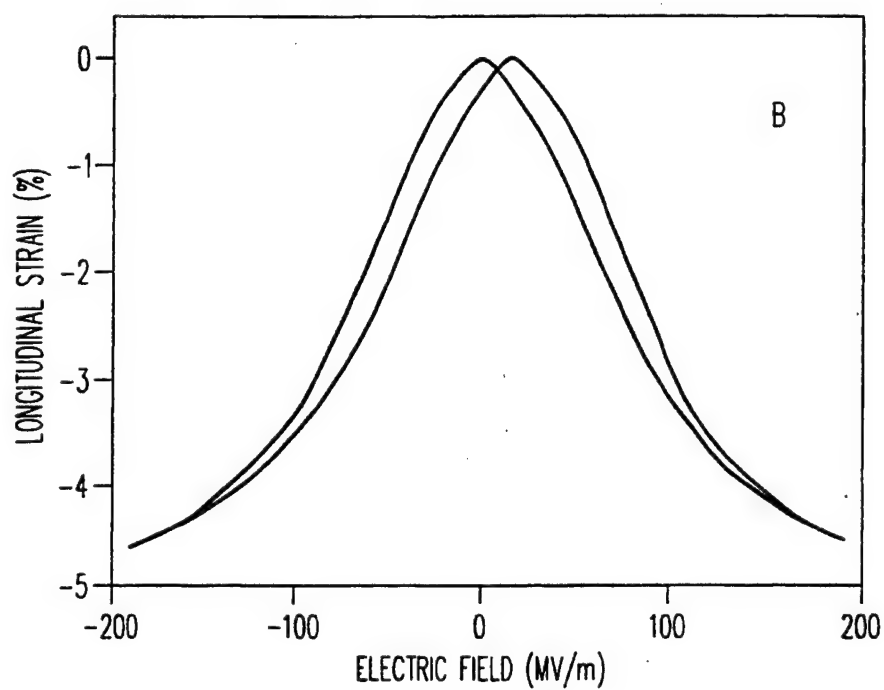
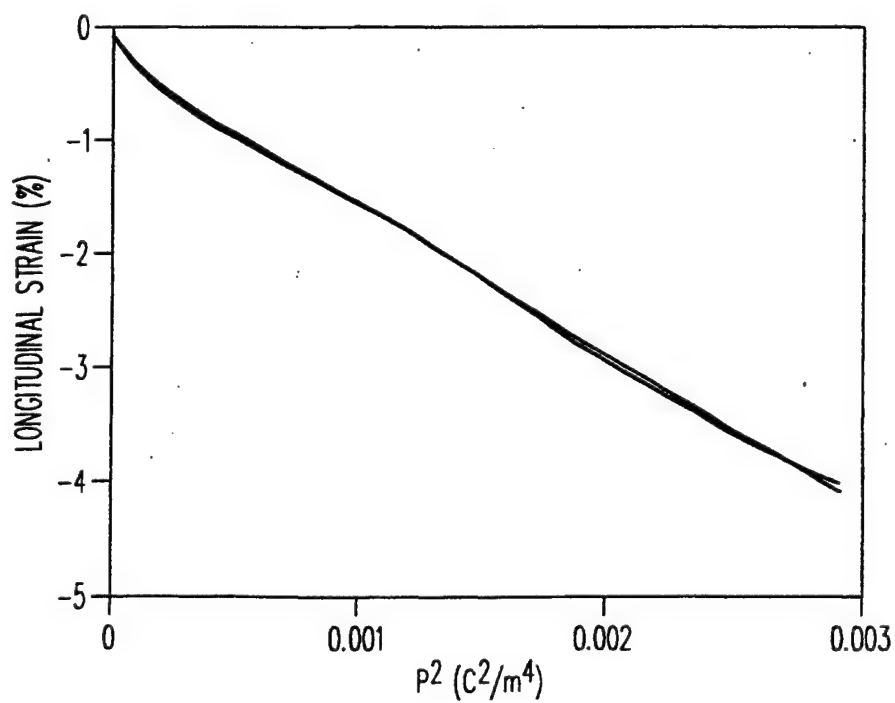
(57) **ABSTRACT**

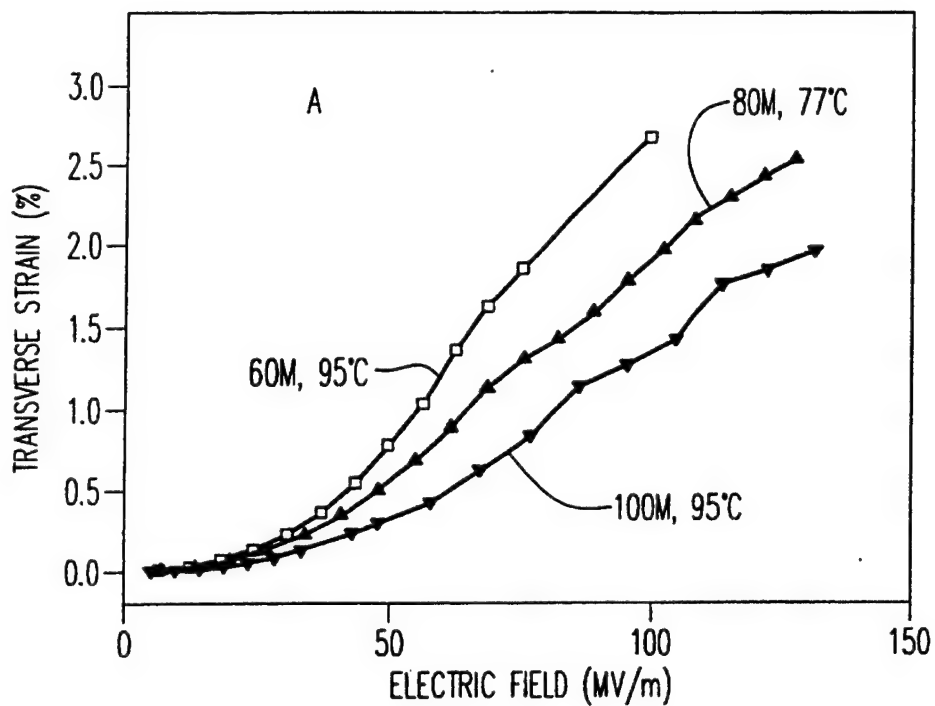
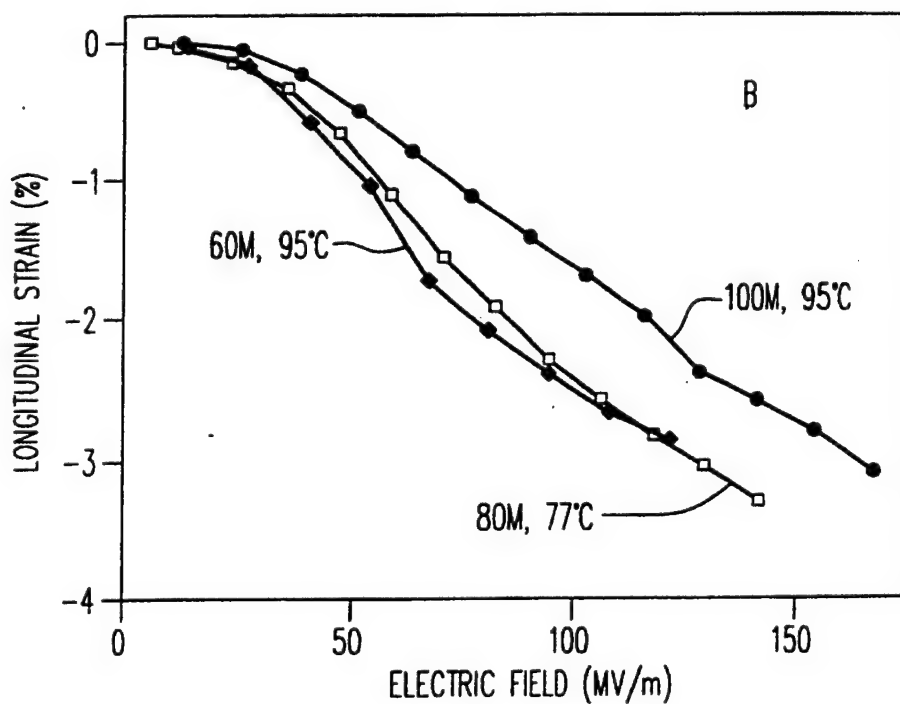
The invention is embodied in an electrical device which
includes at least a layer of a ferroelectric polyvinylidene
fluoride polymer that has been processed to exhibit an
electrostrictive strain of 4% or more when an electric field
gradient of 50 megavolts per meter or greater is applied
thereacross. The processing of the polymer preferably
involves subjecting it to either electron beam radiation or
gamma radiation. The polyvinylidene fluoride polymer is
selected from the group of: polyvinylidene fluoride, polyvi-
nylidene fluoride-trifluoroethylene P(VDF–TrFE), polyviny-
lidene fluoride tetrafluoroethylene P(VDF–TFE), polyviny-
lidene fluoride trifluoroethylene-hexafluoropropylene
P(VDF–TFE–HFE) and polyvinylidene fluoride-
hexafluoropropylene P(VDF–HFE).

27 Claims, 11 Drawing Sheets



**FIG. 1****FIG. 2**

**FIG. 2b****FIG. 3**

**FIG. 4a****FIG. 4b**

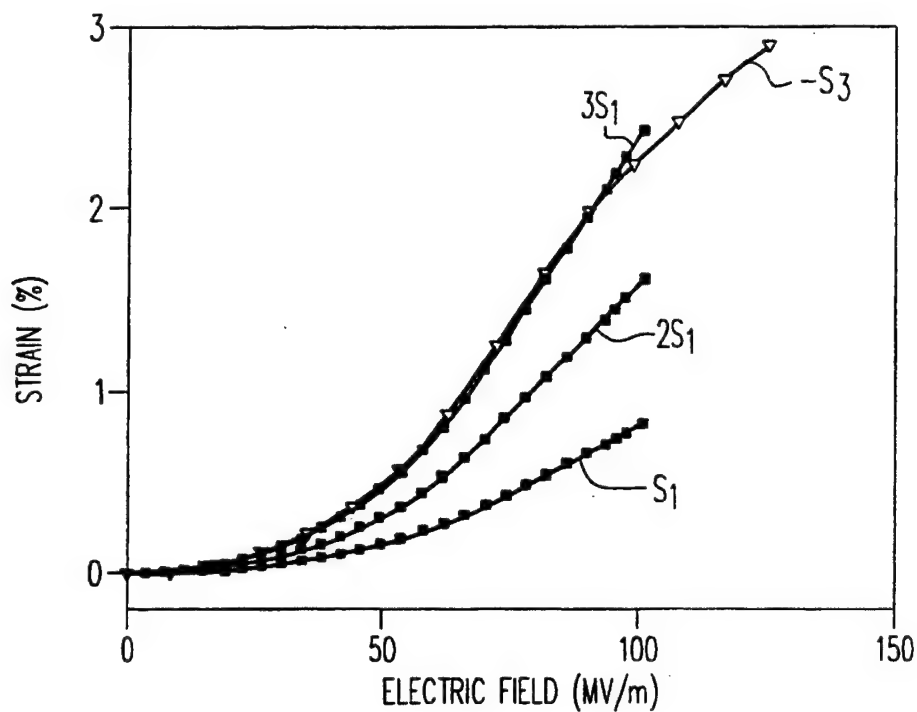
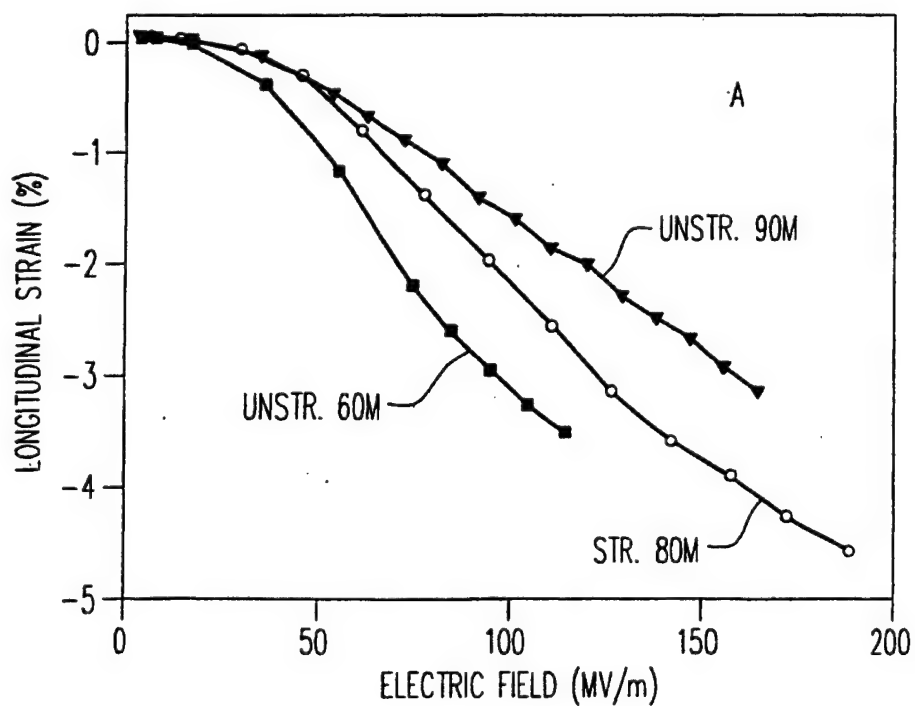
**FIG. 5****FIG. 6**

TABLE 1: COMPARISON OF STRAIN ENERGY DENSITIES

MATERIALS		Y(GPa)	S (%)	$Y_s / 2(J/cm^3)$	$Y_s / 2p(J/kg)$
ELECTROSTRICTIVE	S.	0.40	4.5	0.4	200
PVDF-TrFE	S.	1.3	3.5	0.8	400
PIEZOCERAMICS		64	0.2	0.13	17
MAGNETOSTRICTOR		100	0.2	0.2	21.6
PZN-PT SINGLE CRYSTAL		7.7	1.7	1.0	131
POLYURETHANE		0.017	11	0.1	83

FIG. 7a

TABLE 2: PVDF-TrFE STRETCHED SAMPLES IRRADIATED UNDER NITROGEN ATMOSPHERE

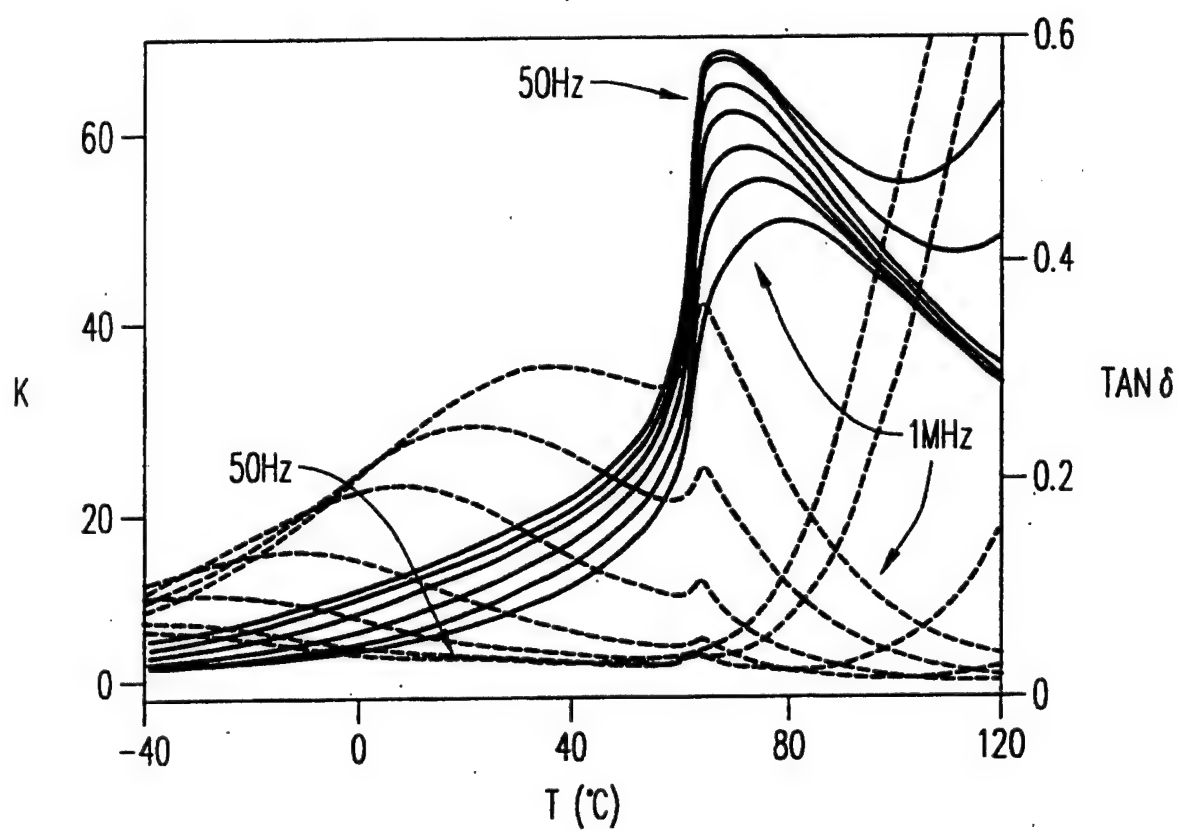
FIELD APPLIED = 150 MV/m		ABSORBED DOSE (Mrad)						
50/50 IRRADIATED AT 77°C		0	40	60	80	100	120	142.5
	$P_r(mC/m^2)$	130.00	-	56.00	43.50	35.50	28.00	-
	$P_r(mC/m^2)$	113.26	-	4.18	2.87	2.55	2.56	-
	$E_r(mV/m)$	54.11	-	8.18	8.01	9.84	13.26	-
50/50 IRRADIATED AT 95°C	$P_r(mC/m^2)$	130.00	63.00	53.00	41.00	32.00	-	-
	$P_r(mC/m^2)$	113.26	54.11	3.54	2.61	3.98	-	-
	$E_r(mV/m)$	54.11	9.72	7.35	7.99	17.71	-	-
65/35 IRRADIATED AT 77°C	$P_r(mC/m^2)$	134.00	-	-	87.00	56.00	50.00	45.5
	$P_r(mC/m^2)$	117.57	-	-	13.18	3.96	2.79	4.0
	$E_r(mV/m)$	53.61	-	-	16.91	9.64	7.53	12.33
65/35 IRRADIATED AT 95°C	$P_r(mC/m^2)$	134.00	-	88.00	60.00	64.00	54.00	-
	$P_r(mC/m^2)$	117.57	-	18.59	3.91	6.54	6.13	-
	$E_r(mV/m)$	53.61	-	18.70	8.55	12.69	13.98	-

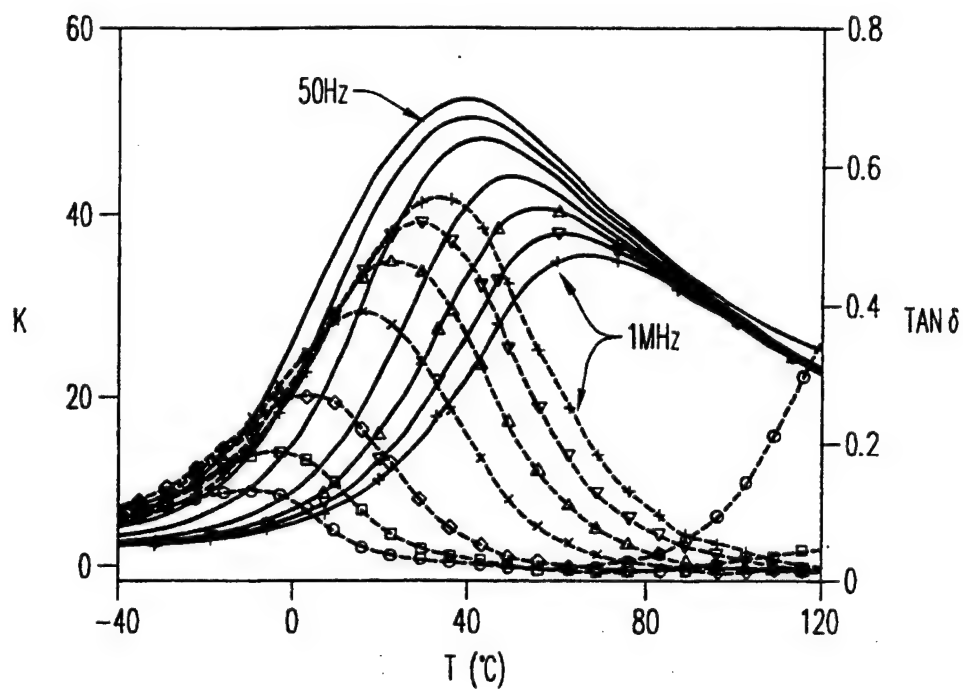
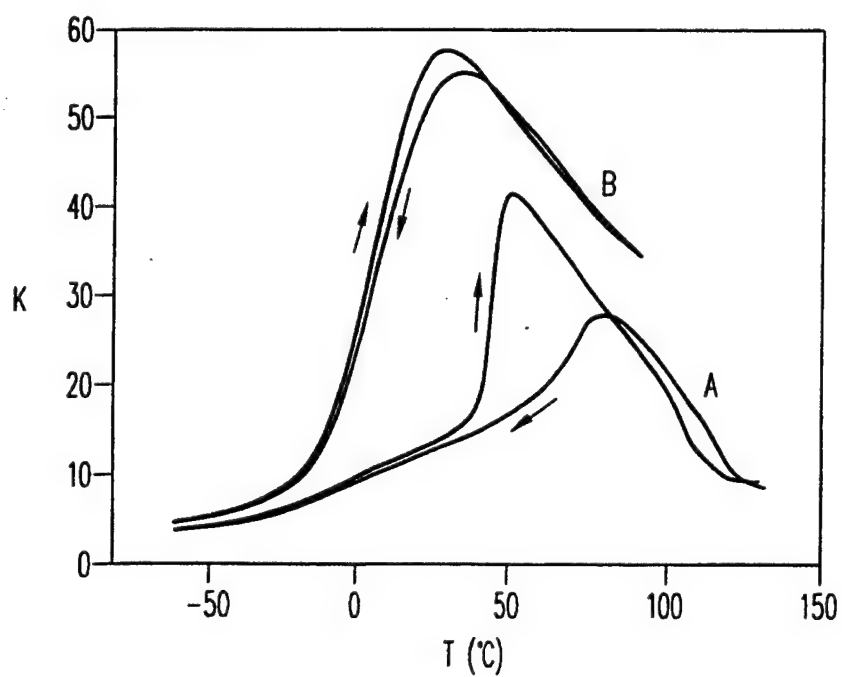
FIG. 7b

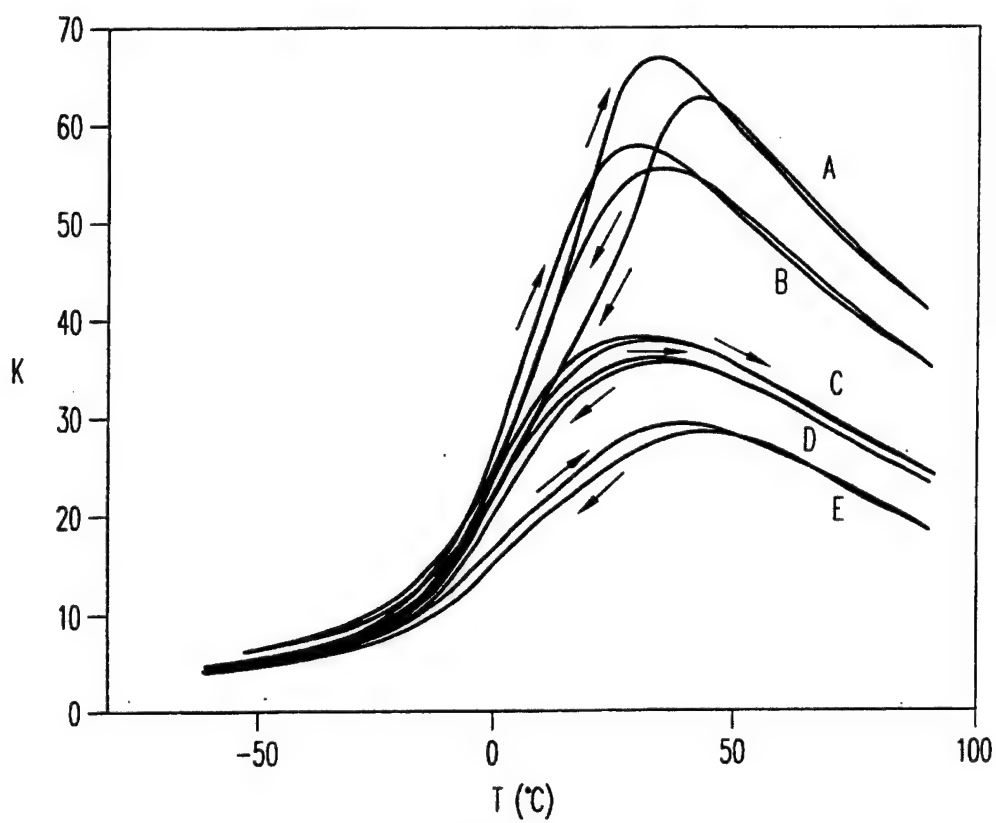
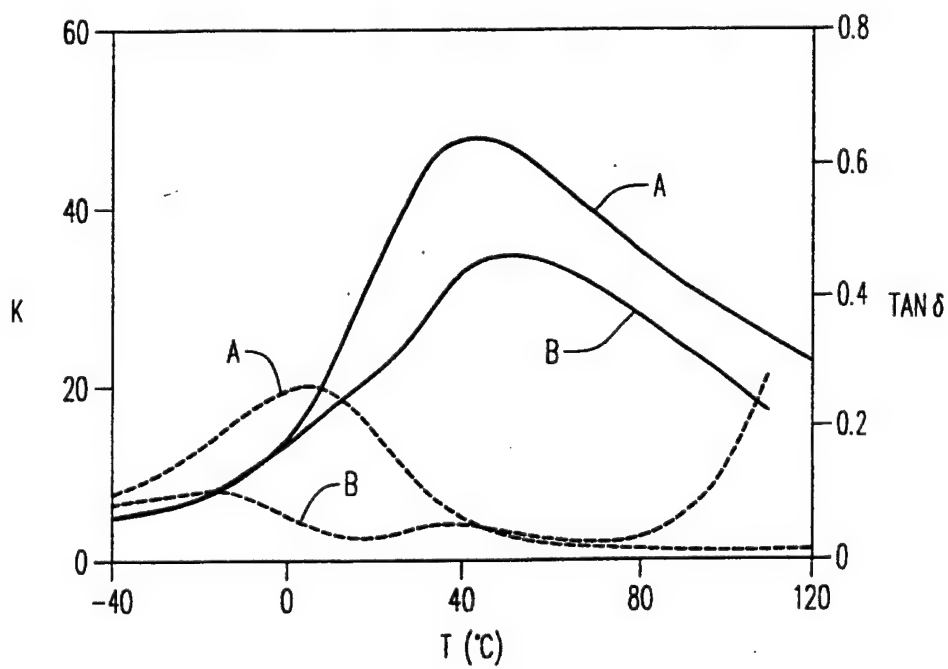
TABLE 3: EFFECT OF IRRADIATION PARAMETERS ON UNSTRETCHED P(VDF-TrFE) COPOLYMER FILMS

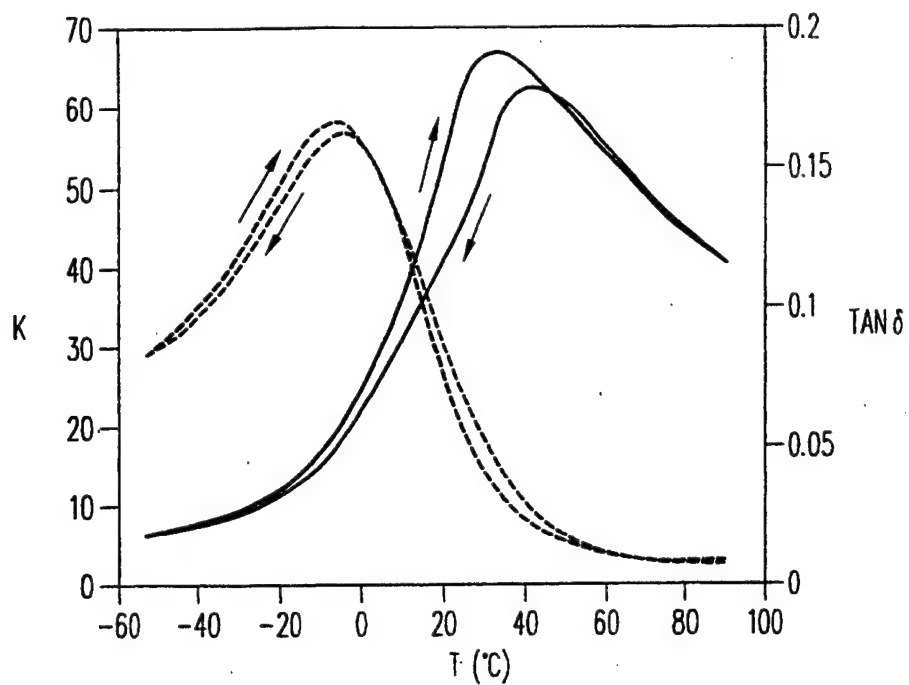
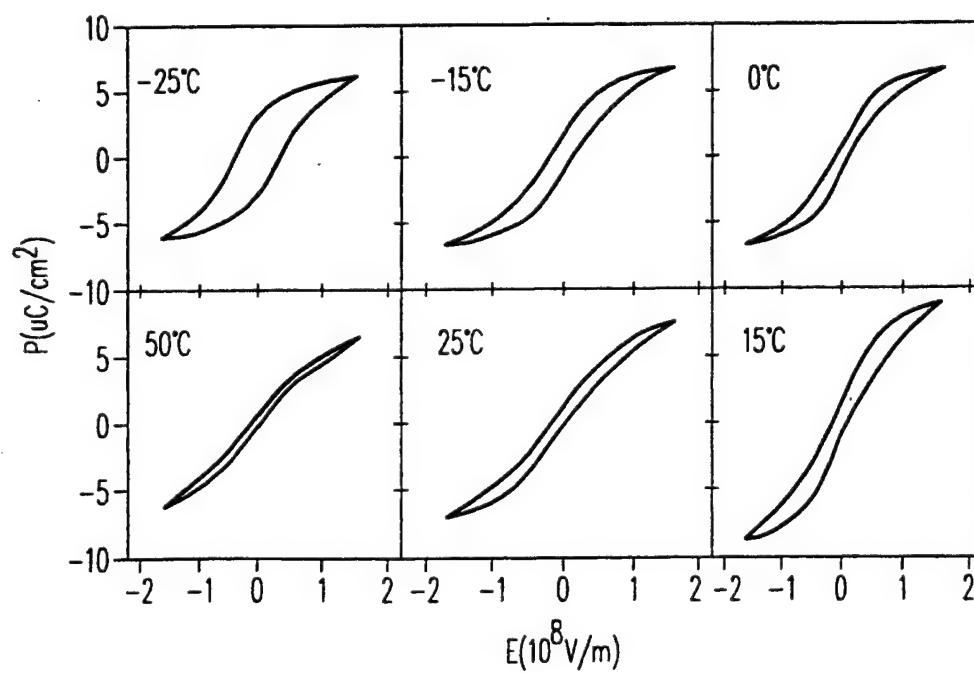
FIELD APPLIED=150 MV/m		ABSORBED DOSE (Mrad)													
		0	30	40	60	80	90	100	110	120	125	142.5	150	175	
50/50 IRRADIATED AT 25°C	P _i (mC/m ²)	87.0				55		62.5		45					
	P _r (mC/m ²)	64.4				3.94		3.0		3.1					
	E _i (mV/m)	44.8				7.2		5.2		8.1					
50/50 IRRADIATED AT 95°C	P _i (mC/m ²)	87.0		52.5	47	35									
	P _r (mC/m ²)	64.4		5.43	4.75	2.34									
	E _i (mV/m)	44.8		10.54	10.89	8.36									
50/50 IRRADIATED AT 120°C	P _i (mC/m ²)	87.0	62.5	54.0	47.5	33	-	31.5	-				20		
	P _r (mC/m ²)	64.4	7.51	3.4	4.90	3.94	-	3.10	-				2.42		
	E _i (mV/m)	44.8	11.2	5.9	10.45	17.54	-	13.59	-				17.36		
65/35 IRRADIATED AT 25°C	P _i (mC/m ²)	105.0						64				65		35	
	P _r (mC/m ²)	86.38						4.3				5.3		1.98	
	E _i (mV/m)	55.41						8.1				8.2		5.7	
65/35 IRRADIATED AT 77°C	P _i (mC/m ²)	105.0	-	-	-	57.00		50.00		46.5	-	40.00	-		
	P _r (mC/m ²)	86.38	-	-	-	6.23		4.32		3.38	-	3.41	-		
	E _i (mV/m)	55.41	-	-	-	13.14		10.17		8.95	-	10.64	-		
65/35 IRRADIATED AT 95°C	P _i (mC/m ²)	105.0	-	-	62.00	60.00		53.00		-	-	-	-		
	P _r (mC/m ²)	86.38	-	-	4.00	5.56		6.05		-	-	-	-		
	E _i (mV/m)	55.41	-	-	7.00	10.78		13.24		-	-	-	-		
65/35 IRRADIATED AT 120°C AR. ATMOSPH.	P _i (mC/m ²)	105.0	-	100.0	66.00	50.00		27.50		-	-	-	-		
	P _r (mC/m ²)	86.38	-	58.03	7.77	3.52		3.38		-	-	-	-		
	E _i (mV/m)	55.41	-	29.52	11.37	7.77		17.55		-	-	-	-		
65/35 SOLUTION CAST IRRADIATED AT 120°C	P _i (mC/m ²)	94.00	72.0	-	75.00	62.50		46.00		-	32.50	-	20.50	20	
	P _r (mC/m ²)	71.22	41.8	-	17.04	7.86		7.41		-	3.69	-	2.01	2.13	
	E _i (mV/m)	55.84	33.2	-	17.55	13.22		17.84		-	16.18	-	15.46	16.3	
72/28 IRRADIATED AT 120°C	P _i (mC/m ²)	100		-	95			47			-	87.0	27.5		
	P _r (mC/m ²)	80.64	-	-	54.26			14.53			-	64.4	2.83		
	E _i (mV/m)	57.38	-	-	37.75			30.79			-	44.8	16.23		
72/28 SOLUTION CAST AT 120°C	P _i (mC/m ²)	100	-	-	80			44			-	-	44		
	P _r (mC/m ²)	80.64	-	-	45.84			13.96			-	-	14.93		
	E _i (mV/m)	57.38	-	-	39.98			35.25			-	-	34.53		

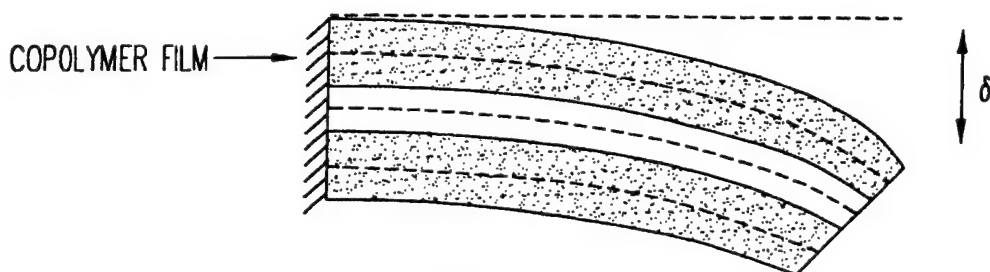
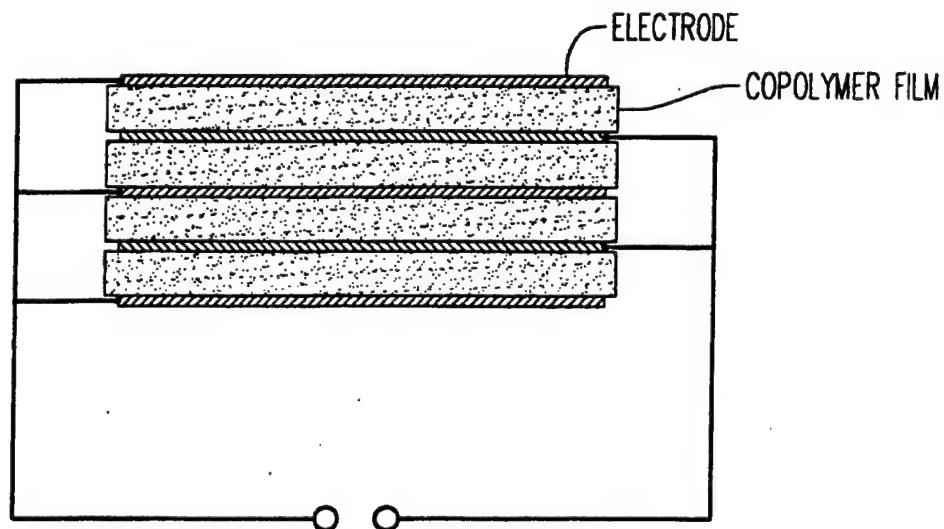
FIG. 7c

**FIG. 8**

**FIG. 9****FIG. 10**

**FIG. 11****FIG. 12**

**FIG. 13****FIG. 14**

**FIG. 15****FIG. 16**

FERROELECTRIC RELAXER POLYMERS

This Application claims priority from U.S. Provisional Application Serial No. 60/065,641, filed Nov. 18, 1997, and Provisional Application Serial No. 60/093,718, filed Jul. 22, 1998.

FIELD OF THE INVENTION

This invention relates to ferroelectric polymers and, more particularly, to relaxor ferroelectric polymers that have been processed to exhibit high electrostrictive strain levels.

BACKGROUND OF THE INVENTION

Ferroelectric polymers have attracted interest for many years as they reveal a new aspect of polymers for use as functional materials. Such polymers have been recognized for their potential uses in a variety of large area transducer, actuator and sensor applications because of their flexibility, mechanical strength, light weight, easy processibility into large area films and ability to be arranged into desirable configurations. By contrast, existing functional materials, such as ceramics, are brittle, heavy and difficult to produce into large area configurations.

In spite of their advantages over the ceramics, current polymers suffer low field sensitivities, such as dielectric constant, piezoelectric coefficient, electromechanical coupling factor and field induced strain. These constraints severely limit the application of ferroelectric polymers as transducers, sensors and actuators.

There is a demand for improved materials for use in actuators and transducers due to the limitations of currently available materials. For example, current actuator materials, such as electrostatic, electromagnetic and piezoelectric materials, exhibit limitations in one or more of the following performance parameters: strain, elastic energy density, speed of response and efficiency. For instance, piezoceramic and magnetostrictive materials, while possessing low hysteresis and high response speeds, suffer from low strain levels (~0.1%). Shape memory alloys generate high strain and high force but are often associated with large hysteresis and very slow response speeds. On the other hand, there are several polymers such as polyurethane, polybutadiene etc. which can generate high electric field induced strain i.e. up to 6-11%. But, due to their low elastic modulus, their elastic energy density is very low. Further, the strain generated in these materials is mainly due to the electrostatic effect, which is a low frequency process. Use of these materials at high frequencies reduces their response drastically. In addition, due to their low dielectric constant, the electric energy density and electromechanical coupling coefficient of these polymers is very low which is an undesirable characteristic for many transducer and actuator applications.

Substantial efforts have been devoted to improvement of phase switching materials where an antiferroelectric and ferroelectric phase change can be field induced to cause a high strain in the material. While strains higher than 0.7% have been achieved in such materials, due to the brittleness of ceramics, severe fatigue has been found to occur at high strain levels. Recently, in a single crystal ferroelectric relaxor, i.e., PZN-PT, an electric field strain of about 1.7%, with very little hysteresis, has been reported, which is exceptionally high for an inorganic materials (see: Park and Shrout, J Appl. Phys., 82, 1804 (1997)). In such ceramic materials, mechanical fatigue occurs at high strain levels, a major obstacle limiting their use for many applications.

For many applications, such as microrobots, artificial muscles, vibration controllers, etc., higher strain levels and

higher energy densities are required. Thus, there is a need for a general purpose electroactive material with improved performance for use with transducer and actuators.

There is a further requirement for improved ultrasonic transducers and sensors for use in medical imaging applications and low frequency acoustic transducers. Current piezoceramic transducer materials, such as PZTs, have a large acoustic impedance ($Z > 35$ Mrayls) mismatch with the air and human tissue ($Z < 2$ Mrayls). On the other hand, piezoelectric polymers such as P(VDF-TrFE), PVDF not only have an acoustic impedance well matched ($Z < 4$ Mrayls) to human tissue but also offer a broad nonresonant frequency bandwidth. But, because of their low piezoelectric activity and low coupling coefficient, the sensitivity of such ultrasonic polymer transducers is very low.

The capacitor industry also requires a capacitor which has a much higher electric energy density than is currently available. Current dielectric materials, such as polymers, have a low dielectric constant (~2-10) and limited energy density. In addition, with current ceramics, the maximum field which can be applied is limited.

Accordingly, it is an object of the invention to provide a polymeric material which can generate a high electric field-induced strain with little hysteresis.

It is another object of the invention to provide a polymeric material which exhibits a high elastic energy density.

It is a further object of the invention to provide a polymer in which the direction of induced strain can be tuned by means of alteration of the ratio of transverse strain (S_1) to longitudinal strain (S_3).

It is yet another object of the invention to provide a polymeric material that exhibits a room temperature dielectric constant that is higher than other currently available polymers.

It is a further object of the invention to provide a polymer which exhibits relaxor ferroelectric behavior and hence has a slim polarization hysteresis loop which, coupled with high electric field breakdown strength, can provide a capacitor with high electric energy density.

SUMMARY OF THE INVENTION

The invention is embodied in an electrical device which includes at least a layer of a ferroelectric polyvinylidene fluoride polymer that has been processed to exhibit an electrostrictive strain of 4% or more when an electric field strength of 50 megavolts per meter or greater is applied thereacross. The processing of the polymer preferably involves subjecting it to either electron beam radiation or gamma radiation. The polyvinylidene fluoride polymer is selected from the group of: polyvinylidene fluoride, polyvinylidene fluoride-trifluoroethylene P(VDF-TrFE), polyvinylidene tetrafluoroethylene P(VDF-TFE), polyvinylidene trifluoroethylene hexafluoropropylene P(VDF-TFE-HFE) and polyvinylidene hexafluoropropylene P(VDF-HFE).

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a plot of polarization P versus electric field E showing polarization hysteresis loops of P(VDF-TrFE) 50/50 copolymer measured at room temperature: (a) before irradiation and (b) Irradiation with 40 Mrad at 120 C.

FIG. 2 is a plot of longitudinal strain versus applied electric field showing the field dependence of P(VDF-TrFE) 65/35 mol % unstretched copolymer film after irradiation at 120 C. with 60 Mrad dose.

FIG. 2b is a plot of longitudinal strain versus applied electric field for P(VDF-TrFE) (50/50 mol %) unstretched film after irradiation at 120 C. with 40 Mrad dose.

3

FIG. 3 is a plot of the electrostrictive relation between the strain and polarization shown in FIG. 2, where the strains at $P > 0$ and $P < 0$ regions are overlapped as a result of the dependence of p_2 on the strain. The deviation of the data points from the straight line at S near zero is due to the zero point uncertainty of the measurement set-up.

FIGS. 4a and 4b illustrate plots of strain versus electric field of P(VDF-TrFE) (65/35 mol %) copolymer films, where plot (B) shows longitudinal strain of stretched film treated the same as in (A). (A) shows transverse strain of stretched films irradiated at different temperatures with different doses.

FIG. 5 is a plot of strain versus electric field of P(VDF-TrFE) (65/35 mol %) unstretched films, irradiated at 120 C. with 60 Mrad dose showing that the longitudinal strain (S_3) is three times higher than transverse strain (S_1).

FIG. 6 illustrates plots of strain versus electric field of P(VDF-TrFE) (65/35 mol %) copolymer films, where plot (A) shows longitudinal strain of stretched and unstretched films irradiated at 120 C. with different doses.

FIG. 7a incorporates Table 1 which indicates effects of irradiation parameters on unstretched P(VDF-TrFE) copolymer films.

FIG. 7b incorporates Table 2 which indicates effects of irradiation parameters on stretched P(VDF-TrFE) copolymer films in a nitrogen atmosphere.

FIG. 7c incorporates Table 3 which compares strain and strain energy densities for a variety of materials.

FIG. 8 is a plot of variation of dielectric constant K (solid lines) and dielectric loss $\tan \delta$ (dashed lines) (50/50 mol %) versus temperature for unstretched, unirradiated copolymer film at 50 Hz, 100 Hz, 1 KHz, 0.1 KHz, 0.4 KHz and 1 MHz frequencies.

FIG. 9 is a plot of variation of dielectric constant K (solid lines) and dielectric loss $\tan \delta$ (dashed lines) as a function of temperature for unstretched P(VDF-TrFE) (50/50 mol %) copolymer films irradiated at 120 C. with 40 Mrad dose. The measuring frequencies (from top to bottom for dielectric constant and from bottom to top for dielectric loss) were 50 Hz, 100 Hz, 1 KHz, 0.1 KHz, 0.4 KHz and 1 MHz.

FIG. 10 is a plot of dielectric constant K measured at 1 kHz with respect to temperature for (A) unirradiated and (B) irradiated stretched, P(VDF-TrFE) (65/35 mol %) copolymer films irradiated at 95 C. with 60 Mrad dose, (where the data were taken during sample heating and cooling).

FIG. 11 is a plot of dielectric constant K versus temperature measured at 1 kHz frequency for stretched P(VDF-TrFE) (65/35 mol %) copolymer films irradiated at 95 C. with (A) 40, (B) 60, (C) 80, (D) 100, (E) 120 Mrad irradiation doses, (where the data were taken during sample heating and cooling).

FIG. 12 is a plot of dielectric constant K (solid lines) and dielectric loss $\tan \delta$ (dashed lines) versus temperature measured at 1 kHz frequency for unstretched P(VDF-TrFE) (50/50 mol %) copolymer films irradiated at (A) 120 C. with 40 Mrad dose (B) 25 C. with 80 Mrad.

FIG. 13 is a plot of dielectric constant K (solid lines) and dielectric loss $\tan \delta$ (dashed lines) as a function of temperature at 1 kHz frequency for stretched P(VDF-TrFE) (65/35 mol %) copolymer films irradiated at 95 C. with 40 Mrad dose, (where the data were taken during sample heating and cooling).

FIG. 14 is a plot of change in polarization hysteresis loops with the noted temperatures for P(VDF-TrFE) (50/50 mol %) copolymer films irradiated at 120 C. with 40 Mrad.

4

FIG. 15 is a schematic of a bimorph actuator employing a polymer processed in accord with the invention.

FIG. 16 is a schematic of a multilayer capacitor employing polymer layers processed in accord with the invention.

DETAILED DESCRIPTION OF THE INVENTION

In ferroelectric polymers such as P(VDF-TrFE), it has been found during structural investigations that large lattice strains and large changes in dimensions are produced when a phase transformation from ferroelectric phase to paraelectric phase occurs. See: T. Furukawa, *Phase Transition*, 18, 143 (1989); K. Tashiro et al.

It has been observed by others in studies of polyvinylidene fluoride-tri-fluoroethylene P(VDF-TrFE) copolymers, that high energy irradiation can convert the ferroelectric phase into a paraelectric phase. See A. J. Lovinger, *Macromolecules*, 18, 910 (1985) and F. Macchi et al., *Nucl. Instr. and Methods in Phys. Res.*, B46, 324 (1990); *Ferroelectrics*, 109, 303 (1990). Macchi et al. observed changes in dielectric constant, elastic properties and thermal expansion after irradiation and correlated their results to changes in crystallinity. *Ferroelectrics*, 57, 297 (1984); T. Yamada et al., *J. Appl. Phys.*, 52, 948 (1981); and A. J. Lovinger et al., *Polymer*, 28, 617 (1987).

In addition, due to the presence of the crystalline phase, the Young's modulus of these polymers is very high and offers high force levels and high energy densities. These results demonstrate that ferroelectric polymers can provide an effective coupling between an applied electric field and a resultant strain response.

However, a problem exists in utilizing the strain associated with phase transformation in existing ferroelectric polymers. In particular, the problem is that the transition is very sharp and occurs at high temperatures. Further, the transition exhibits a large hysteresis.

The information developed by Macchi et al. and Lovinger served as a foundation for Applicants' study that led to this invention. Applicants examined the effects of irradiation on the field induced strain level, the elastic energy density and degree of hysteresis by (i) change of irradiation parameters (such as irradiation dose and temperature), (ii) use of different sample processing techniques (such as melt pressing and solution casting using different solvents, annealing temperature and time) and (iii) use of different mol %'s of P(VDF-TrFE) copolymer. All irradiation of polymers was carried out in inert atmospheres, e.g., nitrogen or argon, to prevent oxidation of the samples.

It was found that under certain sample treatment conditions (irradiation dose, irradiation temperature, film preparation methods etc.), an ultra high electrostrictive strain and a high elastic energy density can be obtained. Tested polymers can withstand an electric field higher than 350 MV/m, resulting in very high elastic energy densities. It was also found that the phase which was transformed after electron irradiation is not a simple paraelectric phase, but a relaxor ferroelectric which has local micropolar regions.

Applicants were able to modify the structure of ferroelectric polymers so that use could be made of the strains associated with phase transition at room temperature and to either reduce or eliminate the hysteresis losses, without reducing the strain levels. It was found that this was possible if the macroscopic coherent polarization domains could be broken up and inhomogeneities/defects introduced into the crystal structure, i.e., conversion of part of the trans molecular bonds to gauche molecular bonds.

There are several ways by which these effects can be accomplished, i.e., chemically, by adding a bulky side group to the main polymer chain which operates as an internal plasticizer; and by irradiation, i.e., by introducing defects using high energy radiation (e.g. at energy levels in an approximate range of 500 KeV to 3 MeV) using beta or gamma rays in an oxygen free atmosphere. The radiation, in addition to inducing defects in the molecular structures, also enabled crosslinking to occur.

In addition to P(VDF-TrFE), it is clear that additional polyvinylidene fluoride polymers such as polyvinylidene fluoride tetrafluoroethylene P(VDF-TFE), polyvinylidene fluoride trifluoroethylene-hexafluoropropylene P(VDF-TFE-HFE), polyvinylidene fluoride-hexafluoropropylene P(VDF-HFE) etc., can be processed to exhibit very high field-induced strains. Hereafter, the term "PVDF" will be used to collectively refer to the aforementioned homopolymer and copolymers.

Using radiation to introduce defects into the polymeric materials, it was found that energy levels in the approximate range of 500 KeV to 3 MeV were usable, although energy levels higher than 500 KeV were preferred. The radiation sources were preferably electron beams, and gamma rays from suitable radioactive species (e.g., cobalt).

Further, it was found that both stretched and unstretched polymeric species exhibited high levels of induced strain, with stretched polymers modified in accord with the invention being preferred for actuator applications with actuation along the stretching direction and unstretched polymers, modified in accord with the invention, being preferred for capacitor applications (along the thickness direction).

Film Preparation and Irradiation Conditions

Polyvinylidene fluoride-trifluoroethylene (P(VDF-TrFE)) copolymers were used during the experimental investigations described below, however it is to be understood that other polymers may be similarly processed to achieve similar results, as indicated above. Copolymer powders having PVDF(x)-TrFE(1-x), where x ranges from 50 to 86 mol %, were supplied by Solvay and Cie, Belgium. Polymer films were prepared by both melt pressing and solution casting methods. In case of melt pressed films, at first, the copolymer powder was pressed between two aluminum foil layers at temperatures between 180 C. to 220 C. and then cooled to room temperature, either by quenching the sandwich in ice cooled liquid or by slow cooling.

For solution cast films, the powder was dissolved either in N,N-dimethyl formamide (DMF) or methyl ethyl ketone (MEK) solutions. These solutions were poured onto an ultrasonically cleaned glass plate, placed in an oven and maintained at 30 C. or 70 C. for six hours, in case of MEK and DMF solutions, respectively. After slow evaporation of the solvents, uniform transparent films of P(VDF-TrFE) were formed.

Stretched films were prepared by uniaxially stretching the films up to five times their initial length, at temperatures between 25 C.-50 C. In order to improve the crystallinity and to remove residual solvent in case of solution cast films, both unstretched and stretched films (under clamped conditions) were annealed in a vacuum oven at 140 C. for 16 hours. The films were then irradiated in an oxygen free atmosphere (e.g., nitrogen or argon) with 2.5 MeV to 3 MeV electrons at different temperature ranges from 25 to 120 C. Several irradiation dosages in the range from 30 to 175 Mrad were used.

Polarization Behavior

It was found that irradiation parameters greatly affected the polymers' material properties. Thus, selection of irra-

diation condition was important to obtain a polymeric material with desired electrical properties. The changes in saturation polarization P_s , remnant polarization P_r and critical field E_c , observed from polarization hysteresis loops measured at room temperature, are shown in FIGS. 7b and 7c (Tables 2 and 3). P_s , P_r and E_c are saturation polarization, remnant polarization and critical field, respectively, observed from ferroelectric hysteresis loops measured at 150 MV/m electric field.

It was discovered that by irradiating the copolymer under proper irradiation conditions, the ferroelectric hysteresis was eliminated. This effect is shown in FIG. 1 which plots polarization P versus electric field E and shows polarization hysteresis loops of P(VDF-TrFE) 50/50 copolymer, measured at room temperature: (a) before irradiation and (b) after irradiation with 40 Mrad at 120 C.

Strain Data

A large increase was observed in electric field-induced strain for both stretched and unstretched films along and perpendicular to the applied electric field (i.e., longitudinal strain S_3 and transverse strain S_1) (along the stretching direction in case of stretched films). FIG. 2b is a plot of longitudinal strain versus applied electric field for a P(VDF-TrFE) (50/50 mol %) unstretched film irradiated with 40 Mrad at 120 C. FIG. 2b is a plot of longitudinal strain versus applied electric field showing the field dependence of P(VDF-TrFE) 65/35 mol % unstretched copolymer film after irradiation at 120 C. with 60 Mrad dose.

As there shown, the maximum longitudinal strain levels, 4% and 4.5 % were observed at 150 and 190 MV/m for P(VDF-TrFE), 50/50 and 65/35 mol % unstretched films respectively. In addition, as shown in FIG. 4, the induced strain exhibited very low hysteresis and followed the electrostrictive relation, $S=Qp^2$ between strain (S) and applied electric field (E). Q is an electrostrictive coefficient. The electrostrictive strain was reproducible under a cyclic electric field. The preferred molar percentages of the monomers in P(VDF-TrFE) are from about 30/70 mol % to about 75/25 mol %.

This attribute is an attractive feature for many transducer applications, for example, displacement transducers are used in optical communications to control optical path lengths with accuracy's on the order of a wavelength of light.

An outstanding characteristic of materials made according to the invention is that by modifying the polymer morphology (stretched vs unstretched) and controlling the irradiation parameters, the magnitude and direction of the transverse and longitudinal strain can be tuned.

For example, for stretched films, the transverse strain is 0.8 to 1.2 times the longitudinal strain. This is shown in FIG. 4 which illustrates plots of strain versus electric field of P(VDF-TrFE) (65/35 mol %) copolymer films, where plot (A) shows longitudinal strain of stretched and unstretched films irradiated at 120 C. with different doses and plot (B) shows transverse strain of stretched films irradiated at different temperatures with different radiation.

In unstretched films, the transverse strain is about 0.2 to 0.4 times the longitudinal strain (with an opposite sign). This is shown in FIG. 5 which is a plot of strain versus electric field of P(VDF-TrFE) (65/35 mol %) unstretched films, irradiated at 120 C. with 60 Mrad dose, showing that longitudinal strain (S_3) is three times higher than transverse strain (S_1).

However, strain measured perpendicular to the stretching and applied field direction is always smaller than the strain measured along the field direction (longitudinal strain, S_3) and the strain measured along the stretching direction (transverse strain, S_1).

The effect of irradiation parameters are shown in FIGS. 4 and 5. As is apparent from FIG. 6 for certain samples, the ratio of the strain level to electric field is higher in comparison to others. The other samples for which the ratio of strain to field was higher were selected for piezoelectric coefficient measurements. The maximum measured piezoelectric coefficients were $d_{33} = -350$ pC/N and $d_{31} = 260$ pC/N. Those measured values are almost 10 times higher than the values reported for prior art P(VDF-TrFE) copolymers and are almost comparable to the piezoelectric ceramic PZT-5H.

A material with such a high piezoelectric coefficient, a high electrostrictive strain level, with a further ability to control the strain magnitude and direction is an attractive candidate for actuator, transducer and sensor applications. However, many soft polymers can also generate very high strain levels due to the electrostatic effect. Therefore, in addition to the strain level, other parameters such as, the volumetric ($Y_{sm}^2/2$) and gravimetric ($Y_{sm}^2/2()$) strain energy densities and blocking force levels should be used in order to evaluate the actuator material's performance.

Table 1 (see FIG. 7a) compares a copolymer prepared in accord with the invention with several currently known materials including the ferroelectric relaxor single crystal PZN-PT, which was discovered recently to possess an ultrahigh strain response. As can be seen, the P(VDF-TrFE) copolymer exhibits the maximum elastic energy density.

Dielectric Results

The dielectric constant of an electrostrictive polymeric material prepared in accord with the invention also shows a remarkable increase at room temperature, after irradiation. FIG. 8 plots variations of dielectric constant K (solid lines) and dielectric loss $\tan \delta$ (dashed lines) versus temperature for unstretched, non-irradiated copolymer film at 50 Hz, 100 Hz, 1 KHz, 0.1 KHz, 0.4 KHz and 1 MHz frequencies. FIG. 9 plots variations of dielectric constant K (solid lines) and dielectric loss $\tan \delta$ (dashed lines) as a function of temperature for unstretched P(VDF-TrFE) (50/50 mol %) copolymer films, irradiated at 120 C. with 40 Mrad dose. The measuring frequencies (from top to bottom for dielectric constant and from bottom to top for dielectric loss) were 50 Hz, 100 Hz, 1 KHz, 0.1 KHz, 0.4 KHz and 1 MHz.

Comparing the non-irradiated material (FIG. 8) and the irradiated material (FIG. 9) the dielectric constant of unstretched 50/50 copolymer, at room temperature, for the irradiated film is higher than the non-irradiated material. After irradiation, the dielectric transition peak becomes broader and shifts towards lower temperatures.

Similar to strain, the dielectric constant also can be adjusted by using different material processing conditions and irradiation parameters. FIG. 10 is a plot of dielectric constant K measured at 1 kHz with respect to temperature for stretched, P(VDF-TrFE) (65/35 mol %) copolymer films (A) unirradiated, (B) irradiated at 95 C. with 60 Mrad dose. As can be seen by comparing the dielectric constant for the unirradiated and irradiated stretched P(VDF-TrFE) (65/35 mol %) film, the dielectric constant for the stretched irradiated films is higher than the unirradiated films.

Again by controlling the irradiation parameters, the dielectric constant can be tailored. FIG. 11 shows this effect and illustrates that by increasing the irradiation dose, the dielectric peak becomes broader, there is less hysteresis and the dielectric constant decreases. Further, as shown in FIG. 12, by increasing the irradiation temperature, the irradiation dose can be reduced significantly.

FIG. 13 illustrates that a maximum dielectric constant of about 67 and a loss in the range of 1-2% was observed at 1

kHz (near room temperature) in 65/35 stretched films irradiated at 95 C. for a 40 Mrad dose.

To Applicants' knowledge, a P(VDF-TrFE) copolymer produced in accord with the invention exhibits a highest dielectric constant (with low dielectric loss at room temperature) among known polymer dielectric materials. The same can be expected for other PVDF polymers.

It was found that a field of up to 350 MV/m can be applied to a polymer prepared in accord with the invention without causing breakdown. Accordingly, a capacitor material results with an electric energy density of about 36 J/cm³.

Relaxor Behavior

Irradiated polymer films prepared in accord with the invention exhibit a relaxor ferroelectric behavior. In comparison to normal ferroelectrics, relaxor ferroelectrics are characterized by the presence of diffuse and rounded maxima in the temperature dependence of their dielectric permittivity, and further exhibit a strong relaxation dispersion for a wide frequency range. In addition, relaxors show a slim polarization hysteresis loop near the dielectric maxima. But, as temperature is reduced from dielectric maxima (T_{max}), the hysteresis loop gradually broadens and finally transforms into a regular rectangular loop at a temperature well below T_{max} .

It was found that irradiated P(VDF-TrFE) shows a broad dielectric peak which shifts towards higher temperature with increasing frequency (see FIG. 9) and follows the Vogel-Fulcher law, an empirical law which is applicable for a system which undergoes relaxation freezing below certain temperatures. The square-to-slim hysteresis loop is evident in FIG. 14 which plots changes in polarization hysteresis with various temperatures for P(VDF-TrFE) (50/50 mol %) copolymer films irradiated at 120 C. with 40 Mrad. As can there be seen, the polarization behavior becomes hysteretic at -25 C., with remnant polarization, $P_r = 2.1$ mC/cm², saturation polarization, $P_s = 40$ mC/cm² and critical field, $E_c = 45.5$ MV/m. However, with increases in temperature, the polarization reduces gradually and shows a slightly a non-linear polarization loop near 50 C. i.e. near T_{max} .

These results show that a material made in accord with the invention (i.e., after irradiation) behaves like a relaxor ferroelectric material (rather than a simple paraelectric, as reported earlier). The results obtained from X-ray scans, Raman spectra, DSC and crosslinking measurements show that electron irradiation breaks up the coherent polarization domains in the normal ferroelectric material to a nanoscale polar region, introduces defects randomly by introducing gauche bonds in long trans-planar polymer chains and causes crosslinking in the crystalline region. Due to large difference in the lattice constant between polar and non polar phases in a P(VDF-TrFE) copolymer, a gradual increase in the polarization with field in the electrostrictive copolymer produces a giant electrostrictive strain and strain energy density.

Electroactive polymer materials developed in accord with the invention show: very high strain (4-5%), high elastic energy density (above 0.3 J/cm³ or 160 J/kg), high dielectric constant with relatively low loss at room temperature (>40 at 1 kHz and a loss <5%), a slim polarization hysteresis loop at room temperature, a high piezoelectric response in a DC biased state and high electric energy density (a breakdown field >350 MV/m).

Most importantly, being a polymeric material, their acoustic impedance levels match human tissue and exhibit no mechanical fatigue at high strain levels. Further, their transverse strain S_1 can be tuned over a large range with respect to their longitudinal strain S_3 . S_1/S_3 can be tuned from 0.2

to more than 1.1. Accordingly, an electrostrictive relaxor ferroelectric polymer prepared in accord with the invention exhibits improved electrical properties that offer substantial improvements in material characteristics required for capacitor, actuator and transducer applications.

FIGS. 15 and 16 illustrate examples of a bimorph actuator and a multilayer capacitor, both of which incorporate polymer layers that have been processed in accord with the invention.

It should be understood that the foregoing description is only illustrative of the invention. Various alternatives and modifications can be devised by those skilled in the art without departing from the invention. Accordingly, the present invention is intended to embrace all such alternatives, modifications and variances which fall within the scope of the appended claims.

What is claimed is:

1. An electrical device including at least a layer of a relaxor ferroelectric polymer that has been processed to exhibit an electrostrictive strain, at room temperature, of 4% or more when an electric field gradient of 100 megavolts per meter or greater is applied thereacross.

2. The electrical device as recited in claim 1, wherein said relaxor ferroelectric polymer comprises a polyvinylidene fluoride homopolymer or dipolymer.

3. The electric device as recited in claim 2, wherein the molar percentages of polyvinylidene fluoride/trifluoroethylene are from about 30/70 to about 75/25 mol %.

4. The electrical device as recited in claim 1, wherein said polyvinylidene fluoride polymer is selected from the group consisting of: polyvinylidene fluoride, polyvinylidene fluoride-trifluoroethylene P(VDF-TrFE), polyvinylidene fluoride-tetrafluoroethylene P(VDF-TFE), polyvinylidene fluoride trifluoroethylene-hexafluoropropylene (VDF-TFE-HFE) and polyvinylidene fluoride-hexafluoropropylene P(VDF-HFE).

5. The electrical device as recited in claim 1, wherein said electrical device is a capacitor.

6. The electrical device as recited in claim 1, wherein said electrical device is an actuator.

7. The electrical device as recited in claim 1 wherein said layer of relaxor ferroelectric polymer exhibits a stretched configuration.

8. The electrical device as recited in claim 1, wherein said relaxor ferroelectric polymer exhibits a dielectric constant and a dielectric loss, at room temperature, of greater than 40 at 1 kHz and higher, and less than 5%, respectively.

9. The electrical device as recited in claim 1, wherein said relaxor ferroelectric polymer exhibits an elastic energy density, at room temperature, of greater than 0.3 Joules/Cm³ or 160 Joules/kg.

10. The electrical device as recited in claim 1, wherein said relaxor ferroelectric polymer exhibits an electric energy density, at room temperature, which enables avoidance of breakdown at applied field levels thereacross of at least 350 magavolts per meter.

11. An electrical device including at least a layer of a relaxor ferroelectric polymer that is prepared by a process comprising the steps of:

a) annealing a polyvinylidene fluoride polymer at a temperature at about 140° C. for about 16 hours; and

b) irradiating said polyvinylidene fluoride polymer in an oxygen free atmosphere with an energy in the range from about 500 KeV to about 3 MeV;

wherein said relaxor ferroelectric polymer exhibits an electrostrictive strain, at room temperature, of 4% or

more when an electric field gradient of 100 megavolts per meter or greater is applied thereacross.

12. A process for preparing a relaxor ferroelectric polymer comprising the steps of:

c) annealing a polyvinylidene fluoride polymer at a temperature at about 130 to about 140° C. for about 16 hours; and

d) irradiating said polyvinylidene fluoride polymer in an oxygen free atmosphere with an energy in the range from about 500 KeV to about 3 MeV to produce a relaxor ferroelectric polymer which exhibits an electrostrictive strain, at room temperature, of 4% or more when an electric field gradient of 100 megavolts per meter or greater is applied thereacross.

13. The process of claim 12, wherein said irradiating step is at a temperature from about 25° C. to about 120° C.

14. The process of claim 12, wherein said polyvinylidene fluoride polymer is selected from the group consisting of: polyvinylidene fluoride homopolymer, polyvinylidene fluoride-trifluoroethylene P(VDF-TrFE), polyvinylidene fluoride-tetrafluoroethylene P(VDF-TFE), polyvinylidene fluoride trifluoroethylene-hexafluoropropylene (VDF-TFE-HFE) and polyvinylidene fluoride-hexafluoropropylene P(VDF-HFE).

15. The process of claim 14, wherein said polyvinylidene fluoride polymer is P(VDF-TrFE).

16. The process of claim 15, wherein the molar percentages of polyvinylidene fluoride/trifluoroethylene are from about 30/70 to about 75/25 mol %.

17. A relaxor ferroelectric polymer prepared by a process comprising the steps of:

a) annealing a polyvinylidene fluoride polymer at a temperature of about 130° C. to about 140° C. for about 16 hours; and

b) irradiating said polyvinylidene fluoride polymer in an oxygen free atmosphere with an energy in the range from about 500 KeV to about 3 MeV to produce a relaxor ferroelectric polymer which exhibits an electrostrictive strain, at room temperature, of 4% or more when an electric field gradient of 100 megavolts per meter or greater is applied thereacross.

18. The relaxor ferroelectric polymer of claim 17, wherein said irradiating step is at a temperature from about 25° C. to about 120° C.

19. The relaxor ferroelectric polymer of claim 17, wherein said polyvinylidene fluoride polymer is selected from the group consisting of: polyvinylidene fluoride homopolymer, polyvinylidene fluoride-trifluoroethylene P(VDF-TrFE), polyvinylidene fluoride-tetrafluoroethylene P(VDF-TFE), polyvinylidene-fluoride trifluoroethylene-hexafluoropropylene (VDF-TFE-HFE) and polyvinylidene fluoride-hexafluoropropylene P(VDF-HFE).

20. The relaxor ferroelectric polymer of claim 19, wherein said polyvinylidene fluoride polymer is P(VDF-TrFE).

21. The relaxor ferroelectric polymer of claim 20, wherein the molar percentages of polyvinylidene fluoride/trifluoroethylene are from about 30/70 to about 75/25 mol %.

22. A relaxor ferroelectric polymer of electrostrictive polyvinylidene fluoride wherein said polymer exhibits an electrostrictive strain, at room temperature, of 4% or more when an electric field gradient of 100 megavolts per meter or greater is applied thereacross.

23. The relaxor ferroelectric polymer of claim 22, wherein said polymer exhibits the following properties: a dielectric constant, at room temperature, of greater than 40 at 1 kHz or higher; a dielectric loss, at room temperature, of less than 5%; and an electric energy density, at room temperature, of

11

greater than 0.3 Joules/cm^3 or 160 Joules/kg , which enables avoidance of breakdown at applied field levels thereacross of at least 350 megavolts per meter.

24. The relaxor ferroelectric polymer of claim 22, wherein said polyvinylidene fluoride polymer is selected from the group consisting of: polyvinylidene fluoride homopolymer, polyvinylidene fluoride-trifluoroethylene P(VDF-TrFE), polyvinylidene fluoride-tetrafluoroethylene P(VDF-TFE), polyvinylidene-fluoride trifluoroethylene-hexafluoropropylene (VDF-TFE-HFE) and polyvinylidene fluoride-hexafluoropropylene P(VDF-HFE).

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25. The relaxor ferroelectric polymer of claim 24, wherein said polymer is polyvinylidene fluoride-trifluoroethylene p(VDF-TrFE).

26. The relaxor ferroelectric polymer of claim 25, wherein the molar percentages of polyvinylidene fluoride/trifluoroethylene are from about 30/70 to about 75/25 mol %.

27. The relaxor ferroelectric polymer of claim 22, wherein said polymer exhibits a stretched configuration.

* * * * *

APPENDIX 2



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May 11, 2001

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RE: U.S. Patent Application Serial No. 10/121,936 (Entitled: High Dielectric Constant Composites of Metallophthalocyanine Oligomer and Poly(vinylidene-trifluoroethylene) Copolymer)
PSU Invention Disclosure No. 2000-2366
"Electromechanical and Dielectric Applications of P(VDF-TrFE) Based Terpolymer Systems"
Inventors: Q. Zhang, H. Xu, Z-Y. Cheng

Sponsored By:

DARPA/ONR Contract No. N00173-99-C-2003 (PSU No. 2000-2366 - Notified ONR of Invention on 5/11/01)

ONR Contract No. N00014-97-1-0900 (PSU No. 97-1833 - Notified ONR of Invention on 2/13/98)
U.S. Patent Application Serial No. 09/195,061
"Ferroelectric Relaxor Copolymers"
Inventors: Q. Zhang and V. Bharti

ONR Contract No N00014-96-1-1173 and N00014-00-1-0623 (PSU No. 2001-2447 - Notified ONR of Invention on 5/24/01) (Provisional Patent Application Serial No. 60/283,755)
"High Dielectric Constant Polymer Systems Based on Metallophthalocyanine and Poly-Vinylidene-trifluorethylene"
Inventors: Q. Zhang, H. Xu and Z-Y. Cheng

Dear Colleague:

Please update your records regarding the referenced PSU invention 2000-2366 to show that a second continuation-in-part patent application was filed on April 12, 2002, Serial No. 10/121,936. The '936 application contains the addition of information contained in U.S. Provisional No. 60/283,755, which covered PSU Inv. Disc. No. 2001-2447, to a U.S. Patent Application No. 10/108,231 (the "231" application). The '231 application relates to PSU Inv. Disc. Nos. 2000-2366 and 97-1833. You should also update your records regarding the 97-1833 and 2001-2447 inventions. The '936 application was sponsored under the Contract Nos. referenced above. Enclosed is a copy of the CIP patent application. We will forward a copy of the patent once it issues.

**HIGH DIELECTRIC CONSTANT COMPOSITES OF
METALLOPHTHALAOCYANINE OLIGOMER AND POLY(VINYLDENE-
TRIFLUOROETHYLENE) COPOLYMER**

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This application claims priority from U.S. Provisional Application No. 60/283,755, filed April 13, 2001, and is a continuation-in-part application of United States Serial No. (not yet assigned), filed March 27, 2002, (Express Mail. No. EV 093432213 US), entitled "Terpolymer Systems for
10 Electromechanical and Dielectric Applications".

The United States Government has certain license rights to the invention that is the subject of this application as a result of the development thereof under ONR Grant Nos. N00014-00-1-0623 and
15 N00014-96-1-1173; under NIH Grant No. 1 RO1 HL65959; and under DARPA Contract No. NOO173-99-C-2003.

BACKGROUND OF THE INVENTION

20

Field of the Invention

The present invention relates to composite materials with elevated electric field induced strain levels, elevated dielectric constants, and
25 having flexible mechanical properties. The materials of the invention comprise a polymer matrix and high dielectric constant organic material.

Description of the Prior Art

30 Because of their many attractive features such as light weight, high mechanical flexibility, and conformability, electroactive polymers are of

great interest for a broad range of applications such as electromechanical and dielectric devices. On the other hand, compared with ceramic materials, the electroactive properties of polymers, such as the dielectric constant and electromechanical response, are not very high. In the past
5 several decades, there has been a great deal of effort to develop polymers with improved functional properties. One of the focuses of these research and development efforts is to raise the dielectric constant of polymers substantially. In addition to applications directly related to capacitors and charge storage devices, a high dielectric constant polymer is also required
10 for high electromechanical responses. The reason behind this is that in the electromechanical transformation process, the mechanical energy output of an electroactive material can't exceed the input electric energy due to the principle of energy conservation. The input electric energy is directly proportional to the dielectric constant of the material and also the
15 square of the applied field. Therefore, in order to develop high performance electroactive polymers for electromechanical applications, one of the key issues is how to substantially raise the dielectric constant of the polymer.

20 Recently, by making use of high energy electron irradiation, it has been shown that the room temperature dielectric constant of poly(vinylidene-trifluoroethylene) copolymer P(VDF-TrFE) can be increased to about 50, a marked improvement compared with the current available polymers. Elevated dielectric constant PVDF-based terpolymer
25 materials are also developed. However, how to raise the dielectric constant to much higher level without stiffening the polymers is still a challenge. For example, using high dielectric constant ceramics as the filler, the room temperature dielectric constant of the so-called 0-3 composites (ceramic powder polymer matrix composites) can reach 300.
30 One of the consequences of this ceramic filling process to the 0-3 composites is to increase the elastic modulus of the composites

significantly above that of the polymer matrix. It is an objective of the present invention to develop alternative 0-3 composite approaches to achieve high dielectric constant while maintain the high flexibility of the matrix. The present invention shows that by making use of the organic solids which possess high dielectric permittivity through the mechanism of nomadic polarization as the fillers, at room temperature and 100 Hz, a composite material with dielectric constant more 1,000 and dielectric loss less than 0.5 can be realized. The composite film is also mechanically flexible with the elastic modulus nearly the same as that of the polymer matrix. In addition, the composite films which elastic modulus is 0.6 GPa also exhibit high strain (~2%) under an electric field of 13 MV/m, a marked improvement compared with other electroactive polymers.

Accordingly, it is an object of the invention to provide polymer matrix materials that exhibit elevated room temperature dielectric constants.

It is another object of the invention to provide polymer matrix materials comprising high dielectric constant material.

It is yet another object of the invention to provide polymer matrix materials having desirable dielectric properties that have mechanical properties similar to their polymer matrix.

These and other objects and advantages of the present invention and equivalents thereof, are achieved by composites useful for electrical applications.

SUMMARY OF THE INVENTION

Using solution casting method, a high dielectric constant composite based on copper-phthalocyanine (CuPc) oligomer and poly(vinylidene fluoride-trifluoroethylene) copolymer is developed. The experimental data show that the low field dielectric constant of the composites (with 55 wt% CuPc) can reach 1,000 and the loss is about 0.5 at room temperature and 100 Hz. Due to the long range electron de-localization in CuPc which results in a strong space charge response of the composite to the external field, there is a strong frequency dispersion of the dielectric properties. In addition, the dielectric properties also exhibit a nonlinear behavior with electric field. One of the uniqueness of the composite is its mechanical properties which remain very much the same as those of the polymer matrix. Even for a composite with 55 wt% CuPc (the volume fraction of CuPc in the composite is also in the similar range), the composite film is still flexible with a Young's modulus of 1.2 GPa at room temperature. Furthermore, it has been demonstrated that in a composite with 40 wt% CuPc filler and relaxor P(VDF-TrFE) matrix, a strain of near 2 % can be induced by a field of 13 MV/m while the composite modulus is 0.6 GPa. The strain is proportional to the square of the applied electric field. In addition to the simple composite approach, other approaches to achieve high dielectric constant with metallophthalocyanine are also discussed.

BRIEF DESCRIPTION OF THE DRAWINGS

25

Fig. 1 shows the molecular structure of copper-phthalocyanine (CuPc).

30

Fig. 2a and Fig 2b are graphs of the dielectric constant and dielectric loss, respectively, of composite films of the invention measured at room temperature. The films have different weight percentage of CuPc filler.

Fig. 3 is a graph of the dielectric properties of composites of the invention having 55 wt% CuPc measured at room temperature in the frequency range from 1 to 100 Hz.

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Figure 4 shows the induced strain of a composite with 40 wt% CuPc filler and the relaxor ferroelectric P(VDF-TrFE) copolymer matrix measured at room temperature and 1 Hz applied field

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Fig. 5a and Fig. 5b are graphs of the dielectric constant and dielectric loss, respectively, of the composite with 55 wt% CuPc filler at different frequencies.

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Fig. 6 shows the molecular structure of ClAn/Cl₄ and Pyrene/0-iodoBA.

DETAILED DESCRIPTION OF THE INVENTION

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The present invention is directed to a polymer based material with preferred, but not necessarily limited to, dielectric constant of higher than 400 while still retaining the flexibility of the polymers, with elastic modulus in the range of polymers (~1 GPa). This class of material has been shown to exhibit high electromechanical properties under low applied field (<20 V/μm).

25

In electroactive materials, it is well known that when an electric field E is applied to a material with the dielectric constant K and elastic modulus Y, there is an electrostatic force (Maxwell stress) generated strain S:

30

$$S = K\epsilon_0 E^2 / Y$$

where $\epsilon_0 = 8.85 \times 10^{-12}$ F/m. In addition, the electromechanical conversion efficient of a Maxwell stress based material is also proportional to KE^2/Y . In current polymers, because of low dielectric constant (<10), in order to generate large Maxwell strain with high energy conversion efficiency, a material which is very soft (low elastic modulus and in most of the current soft polymers with high strain, the modulus is at or below 10 MPa level) and a very high electric field (>100 V/ μ m) are required. For almost all practical device applications, it is necessary to reduce the applied field and use polymer systems with a reasonable elastic modulus (~ 1 GPa). In order to reach those goals, it is clear from eq. (1) that one should significantly raise the dielectric constant of the material.

Recently, it was also discovered that in modified poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE) based polymers, a high electrostrictive strain with high elastic energy density can be achieved (for example 5% strain under 150 V/ μ m field). One of the issues to further improve the performance of the material is to reduce the driving electric field markedly while still maintain the high strain and high elastic energy density.

Metallophthalocyanine oligomers such as copper-phthalocyanine (CuPc) have been shown to exhibit high dielectric constant ($>1,000$) and high dielectric loss while elastically is relatively compliant. One of the problems with CuPc is the poor processibility. Recently, it has also been shown that poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE) based polymers, through proper modifications such as high energy irradiation and terpolymers with selected ter-monomers, exhibit relatively high room temperature dielectric constant (>50) which is by far the highest among the all polymers known and high electrostrictive strain. Therefore, by forming CuPc/PVDF-TrFE composites, one can make use of the very high dielectric constant of CuPc while blocking the dielectric loss due to the

high insulation nature of PVDF-TrFE. Furthermore, PVDF-TrFE as the matrix material can also provide good processing capability which also has relatively high dielectric constant and high field induced strain.

5 Modified poly(vinylidene fluoride-trifluoroethylene) (PVDF-TrFE)
based polymers. Ferroelectric polyvinylidene fluoride polymer, that has
 been processed to exhibit an electrostrictive strain of 4% or more when an
 electric field strength of 50 megavolts per meter or greater is applied
 thereacross, has been developed. The processing of the polymer
 10 preferably involves subjecting it to either electron beam radiation or
 gamma radiation. The polyvinylidene fluoride polymer is selected from the
 group of: polyvinylidene fluoride, polyvinylidene fluoride-trifluoroethylene
 P(VDF-TrFE), polyvinylidene tetrafluoroethylene P(VDF-TFE),
 polyvinylidene trifluoroethylene hexafluoropropylene P(VDF-TFE-HFE) and
 15 polyvinylidene hexafluoropropylene P(VDF-HFE). Such ferroelectric
 polymers can be prepared by a process comprising the steps of
 annealing a polyvinylidene fluoride polymer at a temperature at or about
 130°C to about 140° C for about 16 hours; and irradiating said
 polyvinylidene fluoride polymer in an oxygen free atmosphere with an
 20 energy in the range from about 500 KeV to about 3 MeV to produce a
 relaxor ferroelectric polymer which exhibits an electrostrictive strain, at
 room temperature, of 3% or more when an electric field gradient of about
 100 megavolts per meter or greater is applied thereacross. The
 irradiating step is preferably at a temperature from about 25°C to about
 25 120°C.

Relaxor ferroelectric polymers (polyvinylidene fluoride polymers)
 are preferably selected from the group consisting of: polyvinylidene fluoride
 homopolymer, polyvinylidene fluoride-trifluoroethylene P(VDF-TrFE),
 30 polyvinylidene fluoride-tetrafluoroethylene P(VDF-TFE), polyvinylidene-
 fluoride trifluoroethylene-hexafluoropropylene (VDF-TFE-HFE) and

polyvinylidene fluoride-hexafluoropropylene P(VDF-HFE). In a preferred relaxor ferroelectric polymer the molar percentages of polyvinylidene fluoride/trifluoroethylene are from about 30/70 to about 75/25 mol%.

5 Preferred relaxor ferroelectric polymers of electrostrictive polyvinylidene fluoride exhibit an electrostrictive strain, at room temperature, of 3% or more when an electric field gradient of 100 megavolts per meter or greater is applied thereacross. Such relaxor ferroelectric polymers generally exhibit the following properties: a
10 dielectric constant, at room temperature, of greater than 40 at 1 kHz or higher; and an electric energy density, at room temperature, of greater than 0.3 Joules/cm³ or 160 Joules/kg, which enables avoidance of breakdown at applied field levels thereacross of at least 350 megavolts per meter.

15

Terpolymers exhibiting high room temperature dielectric constant and high strain. Polymers are prepared by polymerizing a mixture of three monomers comprising: at least one monomer of vinylidene-fluoride; at least one monomer selected from the group consisting of
20 trifluoroethylene and tetrafluoroethylene; and at least one monomer selected from the group consisting of tetrafluoroethylene, vinyl fluoride, perfluoro (methyl vinyl ether); bromotrifluoroethylene, chlorofluoroethylene, chlorotrifluoroethylene, and hexafluoroethylene. Polymers of the invention exhibit an electrostrictive strain, at room temperature, of 3% or more when
25 an electric field gradient of 100 megavolts per meter or greater is applied thereacross; exhibit a dielectric constant, at room temperature, of 40 or higher at 1 kHz; and exhibit an elastic energy density, at room temperature, of 0.3 joules/cm³ or higher, or any combinations thereof.

30 Terpolymer process. Also, terpolymers may be prepared by a process comprising: polymerizing a mixture of three monomers

comprising at least one monomer of vinylidene-fluoride; at least one monomer selected from the group consisting of trifluoroethylene and tetrafluoroethylene; and at least one monomer selected from the group consisting of tetrafluoroethylene, vinyl fluoride, perfluoro (methyl vinyl ether), bromotrifluoroethylene, chlorofluoroethylene, chlorotrifluoroethylene, and hexafluoroethylene; stretching said polymer greater than its original length; and thereafter annealing said polymer at a temperature below its melting point, wherein said polymer exhibits an electrostrictive strain, at room temperature, of 3% or more when an electric field gradient of 100 megavolts per meter or greater is applied thereacross, exhibits a dielectric constant, at room temperature, of 40 or higher at 1 kHz, and exhibits an elastic energy density, at room temperature, of 0.3 joules/cm³ or higher, or any combinations thereof.

Ter-polymers include, but are not necessarily limited to, polyvinylidene fluoride-trifluoroethylene-chlorofluoroethylene P(VDF-TrFE-CFE), polyvinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene P(VDF-TrFE-CTFE), polyvinylidene fluoride-tetrafluoroethylene-chlorotrifluoroethylene, polyvinylidene fluoride-trifluoroethylene-hexafluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-hexafluoroethylene, polyvinylidene fluoride-trifluoroethylene-tetrafluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-tetrafluoroethylene, polyvinylidene fluoride-trifluoroethylene-vinyl fluoride, polyvinylidene fluoride-tetrafluoroethylene-vinyl fluoride, polyvinylidene fluoride-trifluoroethylene-perfluoro(methyl vinyl ether), polyvinylidene fluoride-tetrafluoroethylene-perfluoro(methyl vinyl ether), polyvinylidene fluoride-trifluoroethylene-bromotrifluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-bromotrifluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-chlorofluoroethylene, polyvinylidene fluoride-trifluoroethylene-vinylidene chloride, and polyvinylidene fluoride-tetrafluoroethylene-vinylidene chloride

Presented in Figure 2 is the dielectric constant and loss as a function of the frequency (100 Hz to 100 kHz) measured at room temperature for the composite films containing different CuPc wt%. These results show that the composite films possess high dielectric constant. At 100Hz and room temperature, the dielectric constant of the composite with 55 wt% CuPc is about 1,000. And even up to 10 kHz, the dielectric constant of the composite with 55 wt% CuPc is still above 500. In the same frequency range, the dielectric loss varies around 0.5, a significant reduction compared with pure CuPc. For the composite film with 80 wt% CuPc, the loss is high at lower frequencies and then decreases as the frequency increases. The results suggest that the conduction behavior of CuPc also contributes to the dielectric response and for composites at high CuPc wt%, there exist resistance percolation.

The dielectric constant of the composite with 55 wt% CuPc was also characterized at lower frequencies (1 Hz to 100 Hz) and the result is shown in Figure 3. The dielectric constant increases continuously as the frequency decreases, and at 1 Hz it reaches 3,000 although the dielectric loss also becomes quite high (~3). These results indicate that the dielectric properties of the composite have strong frequency dispersion, which is a result of the space charge polarization mechanism in CuPc.

The high dielectric constant of CuPc can be explained in terms of the long-range electron orbital delocalization, also called nomadic polarization. Metallophthalocyanine oligomers are highly conjugated and have a large planar structure. The π -electrons are completely delocalized over the entire molecule. In addition, with increased field, there is also an increased probability of electron tunneling between molecules, resulting in a higher dielectric constant and loss. After mixing with P(VDF-TrFE) matrix, the nomadic polarization of CuPc still plays an important role in the composite film, especially for the composite with high percentage of CuPc.

The composite prepared here also exhibits a high field induced strain, which is proportional to the square of the applied electric field E . Under a field of 10 kV/cm, a strain of 0.3% has been achieved. In the current composites with 55 wt% CuPc, the breakdown field is at about 10 kV/cm (1 MV/m). Therefore, by improving the breakdown field, this composite should exhibit a very high strain response under a relatively low field (10 MV/m, for example). Indeed, a 40wt% CuPc composite which was electron irradiated (30 Mrads at 100 °C) exhibits a field induced strain of near 2% under an applied electric field of 13 MV/m (Figure 4) and the modulus of the composite is 0.6 GPa.

The temperature dependence of the low field dielectric constant and dielectric loss of the composite with 55 wt% CuPc was also investigated and the results are shown in Figure 5. The data shows that over a relatively broad temperature range, the dielectric constant is quite high, especially at lower frequency, e.g., 100Hz. A dielectric maximum of about 2,300 (at 100 Hz) was observed at 70°C, which is near the Curie temperature of P(VDF-TrFE) copolymer. For the non-irradiated copolymer, the dielectric constant is 17 at room temperature and 100 Hz and increase with temperature. At the ferroelectric-paraelectric phase transition temperature, which is about 70 °C for the copolymer studied in this article, the copolymer exhibits a dielectric maximum, which is about 50. Therefore the dielectric constant of the composite, which is determined by copolymer and CuPc, also show a dielectric maximum. This is consistent with the results presented in Figure 5.

In addition to the metallophthalocyanine as the high dielectric constant filler, there are several other classes of high dielectric constant organic molecules, whose polarization is also based on delocalized electrons, which can also be used as filler: ClAn/Cl₄Pa and Pyrene/o-iodoBA, whose molecular structures are illustrated in Figure 6.

In addition to the P(VDF-TrFE) copolymer as the matrix, other copolymers with dielectric constant higher than 20 can also be used as the matrix of the composites such as the high energy irradiated P(VDF-TrFE) and P(VDF-TFE) copolymers, the PVDF based terpolymers.

In addition to the metallophthalocyanine as the high dielectric constant filler, there are several other classes of high dielectric constant organic molecules, whose polarization is also based on delocalized electrons, which can also be used as the filler: ClAn/Cl₄Pa, whose molecular structure is illustrated in Fig. 6a (ClAn/Cl₄Pa, $\epsilon_r=240,000$, $\tan\delta=0.831$), and Pyrene/o-iodoBA shown in Fig. 6b (Pyrene/o-iodoBA, $\epsilon_r=4000$, $\tan\delta\sim 0.5$).

Additional approaches for high dielectric constant polymers based on metallophthalocyanine. In addition to the simple mixing approach as presented in the proceeding sections, there are other approaches for dielectric constant polymers based preferably on metallophthalocyanine which can significantly reduce the loss and raise the breakdown field. In these approaches, CuPc will be directly incorporated into polymer chains at the molecular level. In one approach, CuPc oligomer is grafted with soft polymer chain such as polyethylene glycol (PEG). In CuPc molecule, there are 16 carboxyl groups (-COOH) attached to the CuPc conjugated ring. Those groups can react with hydroxyl group (-OH) on the PEG chain. The dielectric property and mechanical property will depend on how many -COOH groups in CuPc are reacted with PEG and the molecular weight of PEG. For the case when the molecular weight of PEG is high enough, the grafted CuPc can be used directly as composite (liquid crystal polymer type).

CuPc can be directly grafted to PVDF-TrFE polymer chain. The advantage here is that PVDF-TrFE has a relatively high dielectric constant compared with other polymers. In this process, the reaction of PVDF-TrFE copolymer in aqueous NaOH with the use of phase transfer catalyst results in dehydrofluorination. As a consequence, -CH=CF- and CF=CF- double bond units will be formed. The copolymers with double bond units are treated further with peroxidate to form hydroxyl (-OH) group. PVDF-TrFE copolymer with -OH group is then grafted on CuPc by means of esterification.

Another approach addresses the issue of raising the breakdown strength of the composites in which the CuPc powder (or other high dielectric constant semiconductor organic molecular solids) is physically mixed with the polymer matrix. By working with small crystallites (for example, nano-size CuPc fillers) and preventing the formation of agglomerates, the effective field across the grain boundaries will be reduced dramatically which can improve the dielectric strength markedly. In addition to ultrasonic stirring to be used in the preparation of the composites to break up any possible agglomerates small amount of suitable surfactants can be added to the composites to improve the dispersion of CuPc (or other high dielectric constant semiconductor organic molecule solids) in the polymer matrix.

Another approach is a blocking layer approach. In this approach a blocking layer (such as one layer of P(VDF-TrFE) based electrostrictive polymer (the terpolymer or high-energy electron irradiated copolymer)) will be coated on the composite layer. The breakdown field of a thin layer of irradiated P(VDF-TrFE) polymer has been measured to be above 300 MV/m for a 20 μm thick film. In this blocking layer approach, the PVDF layer thickness can be $\sim 0.1\mu\text{m}$. Such a thin layer will have a much higher

breakdown field since the breakdown field is inversely proportional to the film thickness due to the avalanche nature of the electric breakdown process. In addition, the thinness of this layer will not affect the dielectric constant of the whole composite very much. The effect of such a blocking
5 layer is very much similar to the principle of the corona poling in which a field much higher than the breakdown field of the sample to be poled can be applied without causing breakdown because of the limit in the current available.

10 Although the present invention describes in detail certain embodiments, it is understood that variations and modifications exist known to those skilled in the art that are within the invention. Accordingly, the present invention is intended to encompass all such alternatives, modifications and variations that are within the scope of the invention as set forth in the following
15 claims.

WHAT IS CLAIMED IS:

1. A composite material comprising:
5 a polymer matrix; and

at least one high-dielectric constant organic material.
- 10 2. The composite of claim 1, wherein said polymer matrix comprises a dielectric constant measured at room temperature of at least 20 when measured in the frequency range from about 1 to about 100Hz.
- 15 3. The composite of claim 1, wherein said high dielectric constant organic material is a semiconductor.
4. The composite of claim 3, wherein said semiconductor has a dielectric constant higher than 1,000.
- 20 5. The composite of claim 1, wherein said high dielectric constant material comprises at least one material selected from the group consisting of high dielectric constant semiconductor organic solids (dielectric constant higher than 1,000), metallophthalocyanine, ClAn/Cl₄Pa, and Pyrene/o-iodoBA.
- 25 6. The composite of claim 1, wherein said composite exhibits mechanical properties about those of said polymer matrix.
5. The composite of claim 1, wherein said polymer matrix is the
30 copolymer P(VDF-TrFE).

8. The composite of claim 1, wherein said polymer matrix comprises at least one ferroelectric polyvinylidene fluoride polymer, that has been processed to exhibit an electrostrictive strain of 3% or more when an electric field strength of 50 megavolts per meter or greater is applied thereacross.

9. The composite of claim 8, wherein said polyvinylidene fluoride polymer is selected from the group of: polyvinylidene fluoride, polyvinylidene fluoride-trifluoroethylene P(VDF-TrFE), polyvinylidene tetrafluoroethylene P(VDF-TFE), polyvinylidene trifluoroethylene hexafluoropropylene P(VDF-TFE-HFE) and polyvinylidene hexafluoropropylene P(VDF-HFE).

10. The composite of claim 9, wherein said polymer exhibits an electrostrictive strain, at room temperature, of 3% or more when an electric field gradient of about 50 megavolts per meter or greater is applied thereacross.

11. The composite of claim 1, wherein said polymer matrix comprises at least one terpolymer comprising: at least one monomer of vinylidene-fluoride; at least one monomer selected from the group consisting of trifluoroethylene and tetrafluoroethylene; and at least one monomer selected from the group consisting of tetrafluoroethylene, vinyl fluoride, perfluoro (methyl vinyl ether); bromotrifluoroethylene, chlorofluoroethylene, chlorotrifluoroethylene, and hexafluoroethylene.

12. The composite of claim 11, wherein said polymer matrix comprises at least one terpolymer selected from the group consisting of: polyvinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene P(VDF-TrFE-CTFE), polyvinylidene fluoride-tetrafluoroethylene-chlorotrifluoroethylene, polyvinylidene fluoride-trifluoroethylene-

hexafluoroethylene P(VDF-TrFE-HFP), polyvinylidene fluoride-tetrafluoroethylene-hexafluoroethylene, polyvinylidene fluoride-trifluoroethylene-tetrafluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-tetrafluoroethylene, polyvinylidene fluoride-
 5 trifluoroethylene-vinyl fluoride, polyvinylidene fluoride-tetrafluoroethylene-vinyl fluoride, polyvinylidene fluoride-trifluoroethylene-perfluoro(methyl vinyl ether), polyvinylidene fluoride-tetrafluoroethylene-perfluoro(methyl vinyl ether), polyvinylidene fluoride-trifluoroethylene-bromotrifluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-bromotrifluoroethylene,
 10 polyvinylidene fluoride-trifluoroethylene-chlorofluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-chlorofluoroethylene, polyvinylidene fluoride-trifluoroethylene-vinylidene chloride, and polyvinylidene fluoride-tetrafluoroethylene-vinylidene chloride.

15 13. The composite of claim 1, wherein said composite comprises particles of high-dielectric constant material suspended in said polymer matrix.

20 14. The composite of claim 13, wherein said particles of high-dielectric constant materials are uniformly distributed in said polymer matrix.

25 15. The composite of claim 1, wherein said polymer matrix is the copolymer P(VDF-TrFE) and said high-dielectric constant material is metallophthalocyanine.

 16. The composite of claim 1, wherein said composite is in the form of a film.

30 17. The composite of claim 1, wherein said polymer matrix and said high-dielectric constant material are chemically bonded.

18. An electrical device comprising at least one layer of the film of claim 16.

5 19. The composite of claim 1, wherein said at least one high-dielectric constant material is present in an amount from about 20 wt% to about 80 wt%, preferably from about 40 wt% to about 60 wt%, of the total weight of the composite.

10 20. A process for preparing a high dielectric constant composite comprising the steps of:

solubilizing a polymer matrix;

15 adding at least one high-dielectric constant organic material to said polymer matrix; and

forming a film.

20 21. The process of claim 20, wherein said high dielectric constant material comprises at least one material selected from the group consisting of high dielectric constant semiconductor organic solids (dielectric constant higher than 1,000), metallophthalocyanine, ClAn/Cl₄Pa, and Pyrene/o-iodoBA.

25 22. The process of claim 20, wherein said polymer matrix comprises at least one ferroelectric polyvinylidene fluoride polymer, that has been processed to exhibit an electrostrictive strain of 3% or more when an electric field strength of 50 megavolts per meter or greater is
30 applied thereacross.

23. The process of claim 22, wherein said polyvinylidene fluoride polymer is selected from the group of: polyvinylidene fluoride, polyvinylidene fluoride-trifluoroethylene P(VDF-TrFE), polyvinylidene tetrafluoroethylene P(VDF-TFE), polyvinylidene trifluoroethylene hexafluoropropylene P(VDF-
5 TFE-HFE) and polyvinylidene hexafluoropropylene P(VDF-HFE).

24. The process of claim 20, wherein said polymer matrix exhibits an electrostrictive strain, at room temperature, of 3% or more when an electric field gradient of about 50 megavolts per meter or greater
10 is applied thereacross.

25. The process of claim 20, wherein said polymer matrix comprises at least one terpolymer comprising: at least one monomer of vinylidene-fluoride; at least one monomer selected from the group
15 consisting of trifluoroethylene and tetrafluoroethylene; and at least one monomer selected from the group consisting of tetrafluoroethylene, vinyl fluoride, perfluoro (methyl vinyl ether); bromotrifluoroethylene, chlorofluoroethylene, chlorotrifluoroethylene, and hexafluoroethylene.

26. The process of claim 20, wherein said polymer matrix comprises at least one terpolymer selected from the group consisting of: polyvinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene P(VDF-TrFE-CTFE), polyvinylidene fluoride-tetrafluoroethylene-chlorotrifluoroethylene, polyvinylidene fluoride-trifluoroethylene-hexafluoroethylene P(VDF-TrFE-HFP), polyvinylidene fluoride-tetrafluoroethylene-hexafluoroethylene, polyvinylidene fluoride-trifluoroethylene-tetrafluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-tetrafluoroethylene, polyvinylidene fluoride-trifluoroethylene-vinyl fluoride, polyvinylidene fluoride-tetrafluoroethylene-vinyl fluoride, polyvinylidene fluoride-trifluoroethylene-perfluoro(methyl vinyl
25 ether), polyvinylidene fluoride-tetrafluoroethylene-perfluoro(methyl vinyl
30 ether), polyvinylidene fluoride-tetrafluoroethylene-perfluoro(methyl vinyl

ether), polyvinylidene fluoride-trifluorethylene-bromotrifluoroethylene, polyvinylidene fluoride-tetrafluorethylene-bromotrifluoroethylene, polyvinylidene fluoride-trifluorethylene-chlorofluoroethylene, polyvinylidene fluoride-tetrafluorethylene-chlorofluoroethylene, polyvinylidene trifluorethylene-vinylidene chloride, and polyvinylidene fluoride-tetrafluorethylene-vinylidene chloride.

27. A high dielectric constant composite material prepared by a process comprising the steps of:

10

solubilizing a polymer;

adding at least one high-dielectric constant organic material to said polymer; and

15

forming a film.

28 The composite material of claim 27, wherein said high dielectric constant material comprises at least one material selected from the group consisting of high dielectric constant semiconductor organic solids (dielectric constant higher than 1,000), metallophthalocyanine, ClAn/Cl₄Pa, and Pyrene/o-iodoBA.

29. The composite material of claim 27, wherein said polymer matrix comprises at least one ferroelectric polyvinylidene fluoride polymer, that has been processed to exhibit an electrostrictive strain of 3% or more when an electric field strength of 50 megavolts per meter or greater is applied thereacross.

30. The composite material of claim 29, wherein said polyvinylidene fluoride polymer is selected from the group of: polyvinylidene

flouride, polyvinylidene flouride-trifluoroethylene P(VDF-TrFE),
polyvinylidene tetrafluoroethylene P(VDF-TFE), polyvinylidene
trifluoroethylene hexafluoropropylene P(VDF-TFE-HFE) and polyvinylidene
hexafluoropropylene P(VDF-HFE).

5

31. The composite material of claim 27, wherein said polymer
matrix comprises at least one terpolymer comprising: at least one
monomer of vinylidene-fluoride; at least one monomer selected from the
group consisting of trifluoroethylene and tetrafluoroethylene; and at least
one monomer selected from the group consisting of tetrafluoroethylene,
vinyl fluoride, perfluoro (methyl vinyl ether); bromotrifluoroethylene,
chlorofluoroethylene, chlorotrifluoroethylene, and hexafluoroethylene.

32. The composite material of claim 31, wherein said polymer
matrix comprises at least one terpolymer selected from the group
consisting of: polyvinylidene fluoride-trifluoroethylene-
chlorotrifluoroethylene P(VDF-TrFE-CTFE), polyvinylidene fluoride-
tetrafluoroethylene-chlorotrifluoroethylene, polyvinylidene fluoride-
trifluoroethylene-hexafluoroethylene P(VDF-TrFE-HFP), polyvinylidene
fluoride-tetrafluoroethylene-hexafluoroethylene, polyvinylidene fluoride-
trifluoroethylene-tetrafluoroethylene, polyvinylidene fluoride-
tetrafluoroethylene-tetrafluoroethylene, polyvinylidene fluoride-
trifluoroethylene-vinyl fluoride, polyvinylidene fluoride-tetrafluoroethylene-
vinyl fluoride, polyvinylidene fluoride-trifluoroethylene-perfluoro(methyl vinyl
ether), polyvinylidene fluoride-tetrafluoroethylene-perfluoro(methyl vinyl
ether), polyvinylidene fluoride-trifluoroethylene-bromotrifluoroethylene,
polyvinylidene fluoride-tetrafluoroethylene-bromotrifluoroethylene,
polyvinylidene fluoride-trifluoroethylene-chlorofluoroethylene, polyvinylidene
fluoride-tetrafluoroethylene-chlorofluoroethylene, polyvinylidene fluoride-

trifluorethylene-vinylidene chloride, and polyvinylidene fluoride-
tetrafluorethylene-vinylidene chloride.

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ABSTRACT OF THE DISCLOSURE

There are disclosed new composite materials having improved
electric field induced strain levels, improved electric constants, and having
10 advantageous mechanical properties for use in electrical devices.

15

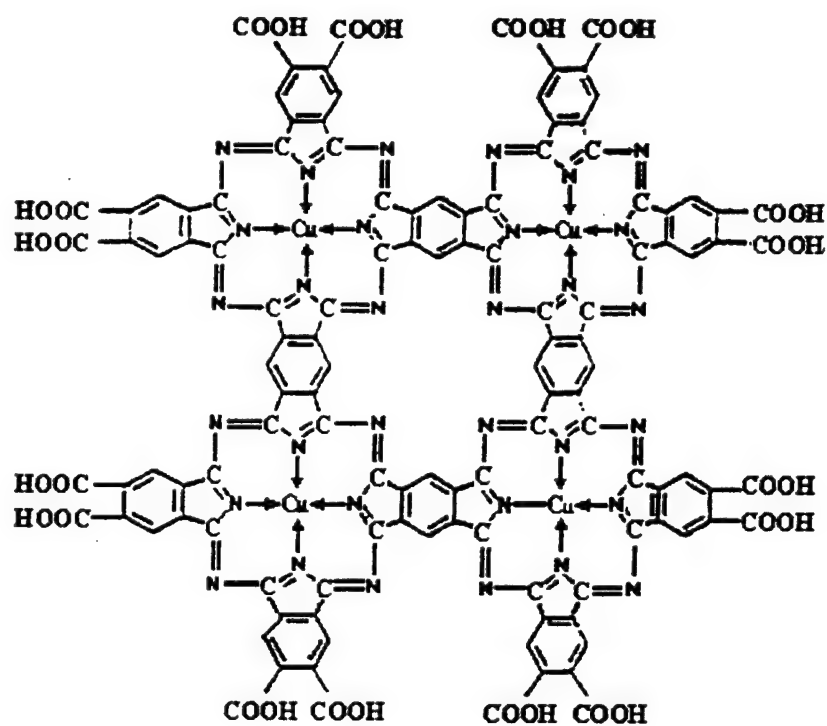


Fig. 1

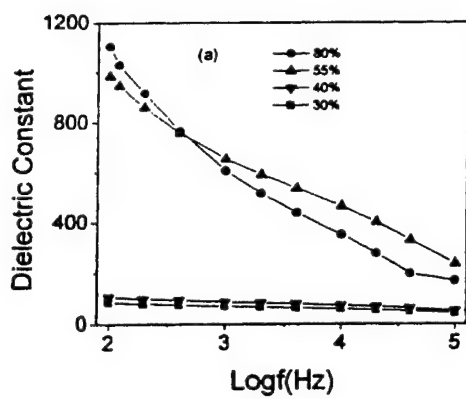


Fig. 2a

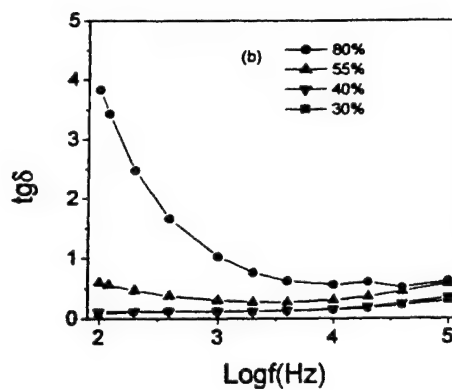


Fig. 2b

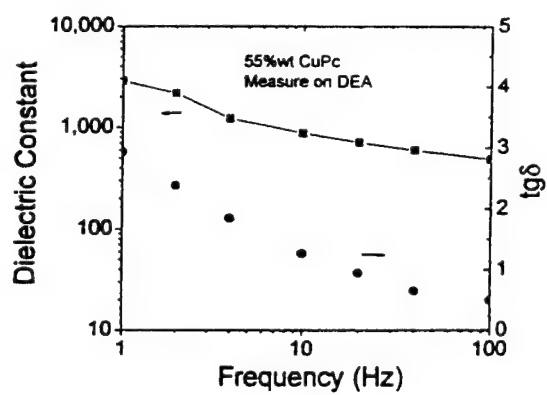


Fig. 3

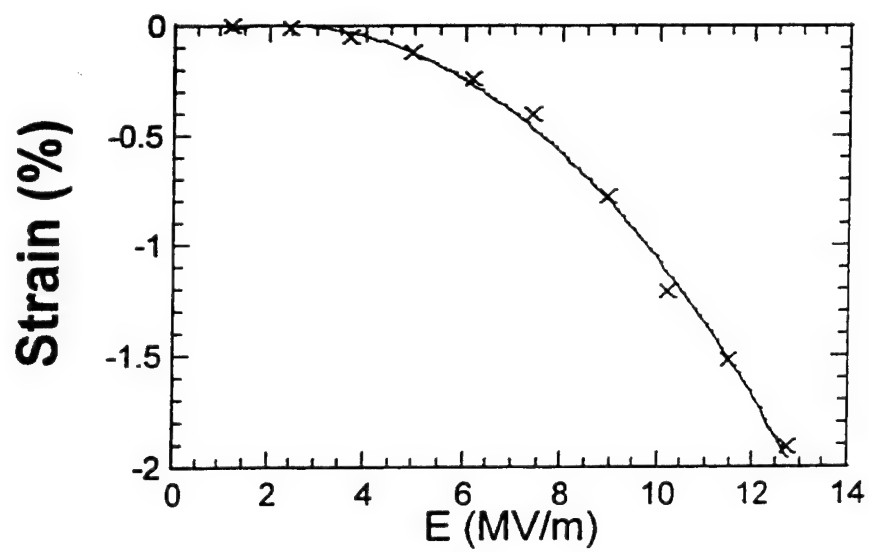


Fig. 4

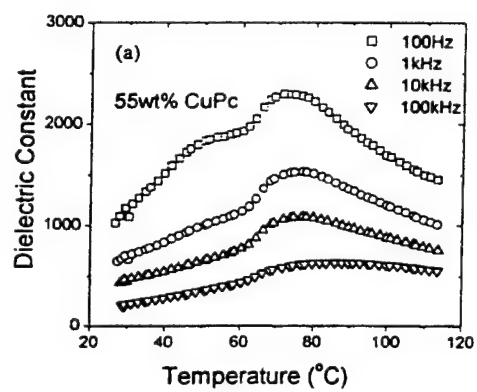


Fig. 5a

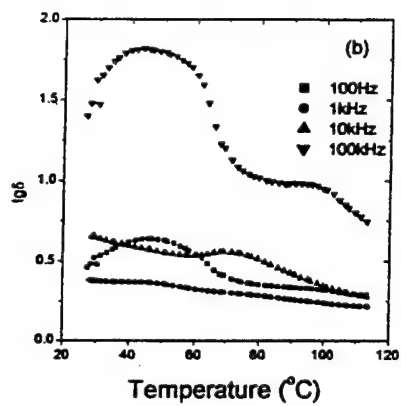


Fig. 5b

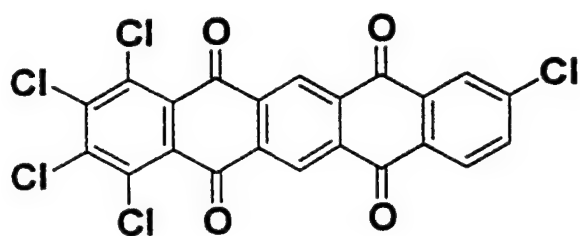


Fig. 6a

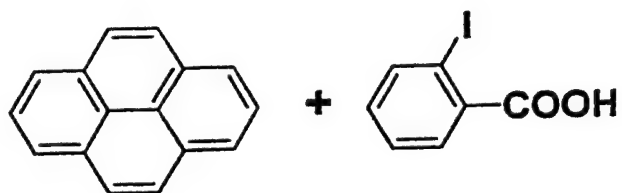


Fig. 6b

APPENDIX 3

PENNSTATE



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June 14, 2002

COPY

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Patent Counsel
Naval Research Laboratory
4555 Overlook Avenue SW
Washington, DC 20375-5320

RE: **U.S. Patent Application Serial No. 10/108,231 (Entitled: 'Terpolymer Systems for Electromechanical & Dielectric Applications')**
PSU Invention Disclosure No. 2000-2366
"Electromechanical and Dielectric Applications of P(VDF-TrFE) Based Terpolymer Systems"
Inventors: Q. Zhang, H. Xu, Z-Y. Cheng

Sponsored By:

DARPA/ONR Contract No. N00173-99-C-2003 (2000-2366 - Notified ONR of Invention on 5/11/01)

ONR Contract No. N00014-97-1-0900 (97-1833 - Notified ONR of Invention on 2/13/98)
U.S. Patent Application Serial No. 09/195,061
"Ferroelectric Relaxor Copolymers"
Inventors: Q. Zhang and V. Bharti

Dear Colleague:

Please update your records regarding the referenced PSU invention 2000-2366 to show that the University elected title to the invention and filed a continuation-in-part patent application on March 27, 2002, Serial No. 10/108,231 (hereinafter the '231 application). This application contains the addition of the information relating to PSU Invention Disclosure Nos. 2000-2366 to the parent application No. 09/195,061, which covers PSU Inv. Disc. No. 97-1833. You should also update your records regarding the 97-1833 invention. The '231 application was sponsored under the Contract Nos. referenced above. Enclosed is a copy of the patent application, along with a Confirmatory Instrument in triplicate. We will forward a copy of the patent once it issues.

A PCT application corresponding to the '231 application was also filed on March 27, 2002, (PCT/US02/09181).

TERPOLYMER SYSTEMS FOR ELECTROMECHANICAL AND DIELECTRIC APPLICATIONS

5

This application claims priority from U.S. Provisional Application No. 60/280,303, filed March 30, 2001, and is a continuation-in-part application of United States Serial No. 09/195,061, filed November 18, 1998.

10

BACKGROUND OF THE INVENTION

Field of the Invention

15

The present invention relates to polymeric materials with elevated electric field induced strain levels, elevated elastic energy densities, and having elevated dielectric constants at room temperature. The material can be used in electromechanical devices which convert electric energy into mechanical energy or convert mechanical energy into electric energy. Material of the invention can also be used as a capacitor which stores electric energy and regulates electric voltage in a circuit.

20

Description of the Prior Art

25

Both polymers and inorganic materials (such as ceramics) have been used widely in electromechanical devices such as actuators, transducers, artificial muscles and robots. However, in the currently available commercial materials, the strain level and elastic energy density both are quite low (strain ~ 0.1% and elastic density ~ 0.1 J/cm³), which causes many problems for device performance. For example, in order to generate large actuation, in many current devices, an amplification scheme has to be used. In addition, the low elastic

30

energy density also reduces the force and power output of the electromechanical devices. In order to improve the performance of a wide variety of electromechanical devices, it is required that the electric field induced strain level and elastic energy density be improved.

5

Polymers are also used widely in capacitors for high voltage operation and charge storage. However, the dielectric constant of the current commercial polymers is quite low (below 10). A high dielectric constant polymer can reduce the capacity volume and charge storage capability of the capacity.

10

In spite of their advantages over the ceramics, current polymers suffer low field sensitivities, such as dielectric constant, piezoelectric coefficient, electromechanical coupling factor and field induced strain. These constraints severely limit the application of ferroelectric polymers as transducers, sensors and actuators.

15

There is a demand for improved materials for use in actuators and transducers due to the limitations of currently available materials. For example, current actuator materials, such as electrostatic, electromagnetic and piezoelectric materials, exhibit limitations in one or more of the following performance parameters: strain, elastic energy density, speed of response and efficiency. For instance, piezoceramic and magnetostrictive materials, while possessing low hysteresis and high response speeds, suffer from low strain levels ($\sim 0.1\%$). Shape memory alloys generate high strain and high force but are often associated with large hysteresis and very slow response speeds. On the other hand, there are several polymers such as polyurethane, polybutadiene etc. which can generate high electric field induced strain i.e. up to 6-11%. But, due to their low elastic modulus, their elastic energy density is very low. Further, the strain generated in these materials is mainly due to the electrostatic effect, which is a low frequency process. Use of these materials at high frequencies

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reduces their response drastically. In addition, due to their low dielectric constant, the electric energy density of these polymers is very low which is an undesirable characteristic for many transducer and actuator applications.

5

Substantial efforts have been devoted to improvement of phase switching materials where an antiferroelectric and ferroelectric phase change can be field induced to cause a high strain in the material. While strains higher than 0.7% have been achieved in such materials, due to the
10 brittleness of ceramics, severe fatigue has been found to occur at high strain levels. Recently, in a single crystal ferroelectric relaxor, i.e., PZN-PT, an electric field strain of about 1.7%, with very little hysteresis, has been reported, which is exceptionally high for an inorganic materials (see: Park and Shrout, J Appl. Phys., 82, 1804 (1997)). In such ceramic
15 materials, mechanical fatigue occurs at high strain levels, a major obstacle limiting their use for many applications.

For many applications, such as microrobots, artificial muscles, vibration controllers, etc., higher strain levels and higher energy densities
20 are required. Thus, there is a need for a general purpose electroactive material with improved performance for use with transducer and actuators.

There is a further requirement for improved ultrasonic transducers and sensors for use in medical imaging applications and low frequency
25 acoustic transducers. Current piezoceramic transducer materials, such as PZTs, have a large acoustic impedance ($Z > 35$ Mrayls) mismatch with the air and human tissue ($Z < 2$ Mrayls). On the other hand, piezoelectric polymers such as P(VDF-TrFE), PVDF not only have an acoustic impedance well matched ($Z < 4$ Mrayls) to human tissue but also offer a
30 broad nonresonant frequency bandwidth. But, because of their low

piezoelectric activity and low coupling coefficient, the sensitivity of such ultrasonic polymer transducers is very low.

5 The capacitor industry also requires a capacitor which has a much higher electric energy density than is currently available. Current dielectric materials, such as polymers, have a low dielectric constant (~2-10) and limited energy density. In addition, with current ceramics, the maximum field which can be applied is limited.

10 Accordingly, it is an object of the invention to provide a polymeric material which can generate a high electric field- induced strain with little hysteresis.

15 It is another object of the invention to provide a polymeric material which exhibits a high elastic energy density.

20 It is yet another object of the invention to provide a polymeric material that exhibits a room temperature dielectric constant that is higher than other currently available polymers.

25 These and other objects and advantages of the present invention and equivalents thereof, are achieved by compositions for electrical or electromechanical devices.

SUMMARY OF THE INVENTION

30 The present invention provides polymers prepared by a polymerizing a mixture of three monomers comprising: at least one monomer of vinylidene-fluoride; at least one monomer selected from the group consisting of trifluoroethylene and tetrafluoroethylene; and

at least one monomer selected from the group consisting of tetrafluoroethylene, vinyl fluoride, perfluoro (methyl vinyl ether); bromotrifluoroethylene, chlorofluoroethylene, chlorotrifluoroethylene, and hexafluoroethylene. Polymers of the invention exhibit an electrostrictive strain, at room temperature, of 3% or more when an electric field gradient of 100 megavolts per meter or greater is applied thereacross, exhibit a dielectric constant, at room temperature, of 40 or higher at 1 kHz, and exhibit an elastic energy density, at room temperature, of 0.3 joules/cm³ or higher, or any combinations thereof.

10

The present invention also provides a process for the preparation of polymers comprising: polymerizing a mixture of three monomers comprising at least one monomer of vinylidene-fluoride; at least one monomer selected from the group consisting of trifluoroethylene and tetrafluoroethylene; and at least one monomer selected from the group consisting of tetrafluoroethylene, vinyl fluoride, perfluoro (methyl vinyl ether), bromotrifluoroethylene, chlorofluoroethylene, chlorotrifluoroethylene, and hexafluoroethylene; stretching said polymer greater than its original length; and thereafter annealing said polymer at a temperature below its melting point, wherein said polymer exhibits an electrostrictive strain, at room temperature, of 3% or more when an electric field gradient of 100 megavolts per meter or greater is applied thereacross, exhibits a dielectric constant, at room temperature, of 40 or higher at 1 kHz, and exhibits an elastic energy density, at room temperature, of 0.3 joules/cm³ or higher, or any combinations thereof.

Also provided are electrical or electromechanical devices comprising at least one layer of a polymer of the invention. Polymers include, but are not necessarily limited to, polyvinylidene fluoride-trifluoroethylene-chlorofluoroethylene P(VDF-TrFE-CFE), polyvinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene P(VDF-TrFE-CTFE),

polyvinylidene fluoride-tetrafluoroethylene-chlorotrifluoroethylene,
 polyvinylidene fluoride-trifluoroethylene-hexafluoroethylene, polyvinylidene
 fluoride-tetrafluoroethylene-hexafluoroethylene, polyvinylidene fluoride-
 trifluoroethylene-tetrafluoroethylene, polyvinylidene fluoride-
 5 tetrafluoroethylene-tetrafluoroethylene, polyvinylidene fluoride-
 trifluoroethylene-vinyl fluoride, polyvinylidene fluoride-tetrafluoroethylene-
 vinyl fluoride, polyvinylidene fluoride-trifluoroethylene-perfluoro(methyl vinyl
 ether), polyvinylidene fluoride-tetrafluoroethylene-perfluoro(methyl vinyl
 ether), polyvinylidene fluoride-trifluoroethylene-bromotrifluoroethylene,
 10 polyvinylidene fluoride-tetrafluoroethylene-bromotrifluoroethylene,
 polyvinylidene fluoride-tetrafluoroethylene-chlorofluoroethylene,
 polyvinylidene fluoride-trifluoroethylene-vinylidene chloride, and
 polyvinylidene fluoride-tetrafluoroethylene-vinylidene chloride

15

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph of electric field induced longitudinal strain as a function of
 the applied field amplitude for the terpolymer P(VDF-TrFE-CTFE). The
 20 terpolymer No. 49 is 72.2/17.8/10 mol %; the terpolymer No. 52 is 66/22.5/11.5
 mol %; and the third embodiment of the graph is the terpolymer 58.5/31.5/10
 mol%. All measurements were made at room temperature.

Fig. 2 is a graph of the field induced transverse strain as a function of the
 25 applied field amplitude for the uniaxially stretched terpolymer P(VDF-TrFE-
 CTFE), 63.1/25.4/11.5 mol% measured at room temperature.

Fig. 3 is a graph of the strain hysteresis loop for the terpolymer P(VDF-
 TrFE-CTFE), 58.5/31.5/10 mol%.

30

Fig. 4a and Fig 4b are graphs of the dielectric constant and loss, respectively, as a function of temperature of the terpolymer P(VDF-TrFE-CTFE) in the frequency range from 100 Hz to 1 MHz (dielectric constant: from the top to bottom: 100, 300, 1k, 3k, 10k, 30k, 100k, 300k, and 1MHz) (dielectric loss: from the bottom to top: 100, 300, 1k, 3k, 10k, 30k, 100k, 300k, and 1MHz).

Fig. 5. Is a graph of the field induced longitudinal strain as a function of the applied field amplitude for the terpolymer P(VDF-TrFE-CFE) , 60/36/4 mol% measured at room temperature.

DETAILED DESCRIPTION OF THE INVENTION

It was found that in certain classes of terpolymer systems such as P(VDF-TrFE-CTFE) (poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene)) and P(VDF-TrFE-CFE) (poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene)), an ultrahigh electric field induced strain can be achieved. In P(VDF-TrFE-CTFE), as shown in Fig. 1, a thickness strain of ~4% can be induced. If the terpolymer is mechanically stretched (4 to 5 times of the original length) and annealed afterwards at a temperature 5 to 15 degrees below the melting temperature of the polymer, a large field induced transverse strain (~3%), see Fig. 2, can be obtained. Electrostrictive strains of about 3% or above are preferred. In addition, the terpolymer has an elastic modulus at room temperature of 0.5 GPa, which results in an elastic energy density (per unit volume) ~ 0.4 J/cm³. Preferred elastic energy densities of terpolymers of the invention are ~0.3 J/cm³ or above. Such a large strain with a very low hysteresis (see Fig. 3) is very useful for electromechanical devices.

It was also found that the P(VDF-TrFE-CTFE) terpolymer has a very high room temperature dielectric constant (c.f., Fig. 4), at 100 Hz, the room temperature dielectric constant can be more than 65, which is significantly higher

than any commercial polymers. Dielectric constants of the terpolymers of the invention are preferably 40 or above.

For those applications, the composition of the terpolymer $P(\text{VDF}_x\text{-TrFE}_y\text{-CTFE}_{1-x-y})$ should be: x is in the range of 0.55 – 0.75 and y in the range of 0.15-0.35.

In $P(\text{VDF-TrFE-CFE})$ terpolymer system, as shown in Fig. 5, there is also a large thickness strain induced electrically. In this terpolymer (60/36/4 mol%, $P(\text{VDF}_x\text{-TrFE}_y\text{-CFE}_{1-x-y})$), a relatively high thickness strain (-4.5%) can be induced under a field ~150 MV/m. The terpolymer also exhibits a high elastic modulus ~ 1 GPa which results in an elastic energy density ~ 1 J/cm³, much higher than those in the piezoelectric materials. For this terpolymer system, the composition range of $P(\text{VDF}_x\text{-TrFE}_y\text{-CFE}_{1-x-y})$, x should be in the range of 0.55 – 0.8 and y in the range of 0.15 – 0.4.

The high strain and high elastic energy density discovered in the terpolymer systems here are very attractive because it is well known that polymers can withstand high elastic strains without fatigue. This is a clear advantage over any inorganic material where the fatigue at high mechanical strain is a serious problem for the electromechanical device applications.

The present invention discloses a series of terpolymer systems which preferably exhibit high electric field induced strain with high elastic energy density and also high room temperature dielectric constant. The terpolymer systems include poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene), poly(vinylidene fluoride-trifluoroethylene-vinylidene chloride), poly(vinylidene fluoride-trifluoroethylene-tetrafluoroethylene), poly(vinylidene fluoride-trifluoroethylene-vinyl fluoride), poly(vinylidene fluoride-trifluoroethylene-perfluoro(Methyl vinyl ether)), poly(vinylidene fluoride-trifluoroethylene-bromotrifluoroethylene), poly(vinylidene fluoride-trifluoroethylene-

chlorofluoroethylene), and poly(vinylidene fluoride-trifluorethylene-vinylidene chloride).

5 High strain and high dielectric constant polymer systems, high energy irradiated P(VDF-TrFE) copolymers, have been earlier disclosed. An advantage of the current terpolymer systems is that the irradiation step used with the copolymer systems is eliminated. This saves manufacture cost and improves the reliability and reproducibility of the electroactive polymer systems.

10 Polymers of the present invention are conveniently prepared or synthesized by polymerizing processing known in the art, such as suspension, emulsion, or solutions methods. Three monomers (i.e., VDF, TrFE, CFE) are selected and contacted or mixed in proportion in the presence of a suitable catalyst or initiator. The resultant terpolymer systems should have a convenient
15 molecular weight suitable for use in electrical or electromechanical devices. The molecular weight of the polymer systems of the present invention is not limited. The molecular weight of terpolymers is preferably, but not limited to, higher than about 50,000, more preferably higher than 100,000, and yet more preferably from about 100,000 to about 300,000.

20

Although the present invention describes in detail certain
embodiments, it is understood that variations and modifications exist known to those skilled in the art that are within the invention. Accordingly, the present
25 invention is intended to encompass all such alternatives, modifications and variations that are within the scope of the invention as set forth in the following claims.

5 **WHAT IS CLAIMED IS:**

1. A polymer prepared by a polymerizing a mixture of three monomers comprising:

10 at least one monomer of vinylidene-fluoride;

 at least one monomer selected from the group consisting of trifluoroethylene and tetrafluoroethylene; and

15 at least one monomer selected from the group consisting of tetrafluoroethylene; vinyl fluoride; perfluoro (methyl vinyl ether); bromotrifluoroethylene; chlorofluoroethylene; chlorotrifluoroethylene; and hexafluoroethylene.

20 2. The polymer of claim 1, wherein said polymer is selected from the group consisting of polyvinylidene fluoride-trifluoroethylene-chlorofluoroethylene P(VDF-TrFE-CFE), polyvinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene P(VDF-TrFE-CTFE), polyvinylidene fluoride-tetrafluoroethylene-chlorotrifluoroethylene,
25 polyvinylidene fluoride-trifluoroethylene-hexafluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-hexafluoroethylene, polyvinylidene fluoride-trifluoroethylene-tetrafluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-tetrafluoroethylene, polyvinylidene fluoride-trifluoroethylene-vinyl fluoride, polyvinylidene fluoride-tetrafluoroethylene-vinyl fluoride, polyvinylidene fluoride-trifluoroethylene-perfluoro(methyl vinyl ether), polyvinylidene fluoride-tetrafluoroethylene-perfluoro(methyl vinyl ether), polyvinylidene fluoride-trifluoroethylene-bromotrifluoroethylene,

30

polyvinylidene fluoride-tetrafluoroethylene-bromotrifluoroethylene,
 polyvinylidene fluoride-tetrafluoroethylene-chlorotrifluoroethylene,
 polyvinylidene fluoride-trifluoroethylene-vinylidene chloride, and
 polyvinylidene fluoride-tetrafluoroethylene-vinylidene chloride.

5

3. The polymer of claim 1, wherein said polymer is polyvinylidene
 fluoride-trifluoroethylene-chlorotrifluoroethylene having a ratio of
 monomers represented as $P(\text{VDF}_x\text{-TrFE}_y\text{-CTFE}_{1-x-y})$, wherein x is about
 0.55 to about 0.75, y is about 0.15 to about 0.35.

10

4. The polymer of claim 1, wherein said polymer is polyvinylidene
 fluoride-trifluoroethylene-hexafluoroethylene having a ratio of monomers
 represented as $P(\text{VDF}_x\text{-TrFE}_y\text{-HFP}_{1-x-y})$, wherein x is about 0.55 to about
 0.75, and y is about 0.15 to about 0.4.

15

5. A polymer of claim 1, wherein said polymer exhibits an
 electrostrictive strain, at room temperature, of 3% or more when an
 electric field gradient of 100 megavolts per meter or greater is applied
 thereacross.

20

6. The polymer of claim 5, wherein said polymer is selected from
 the group consisting of polyvinylidene fluoride-trifluoroethylene-
 chlorotrifluoroethylene $P(\text{VDF-TrFE-CFE})$, polyvinylidene fluoride-
 trifluoroethylene-chlorotrifluoroethylene $P(\text{VDF-TrFE-CTFE})$,
 25 polyvinylidene fluoride-tetrafluoroethylene-chlorotrifluoroethylene,
 polyvinylidene fluoride-trifluoroethylene-hexafluoroethylene, polyvinylidene
 fluoride-tetrafluoroethylene-hexafluoroethylene, polyvinylidene fluoride-
 trifluoroethylene-tetrafluoroethylene, polyvinylidene fluoride-
 tetrafluoroethylene-tetrafluoroethylene, polyvinylidene fluoride-
 30 trifluoroethylene-vinyl fluoride, polyvinylidene fluoride-tetrafluoroethylene-
 vinyl fluoride, polyvinylidene fluoride-trifluoroethylene-perfluoro(methyl vinyl

ether), polyvinylidene fluoride-tetrafluorethylene-perfluoro(methyl vinyl ether), polyvinylidene fluoride-trifluorethylene-bromotrifluoroethylene, polyvinylidene fluoride-tetrafluorethylene-bromotrifluoroethylene, polyvinylidene fluoride-tetrafluorethylene-chlorofluoroethylene, 5 polyvinylidene fluoride-trifluorethylene-vinylidene chloride, and polyvinylidene fluoride-tetrafluorethylene-vinylidene chloride.

7. A polymer of claim 1, wherein said polymer exhibits a dielectric constant, at room temperature, of 40 or higher at 1 kHz.

10

8. The polymer of claim 7, wherein said polymer is selected from the group consisting of polyvinylidene fluoride-trifluorethylene-chlorofluoroethylene P(VDF-TrFE-CFE), polyvinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene P(VDF-TrFE-CTFE), 15 polyvinylidene fluoride-tetrafluoroethylene-chlorotrifluoroethylene, polyvinylidene fluoride-trifluorethylene-hexafluoroethylene, polyvinylidene fluoride-tetrafluorethylene-hexafluoroethylene, polyvinylidene fluoride-trifluorethylene-tetrafluoroethylene, polyvinylidene fluoride-tetrafluorethylene-tetrafluoroethylene, polyvinylidene fluoride-trifluorethylene-vinyl fluoride, polyvinylidene fluoride-tetrafluorethylene-vinyl fluoride, polyvinylidene fluoride-trifluorethylene-perfluoro(methyl vinyl ether), polyvinylidene fluoride-tetrafluorethylene-perfluoro(methyl vinyl ether), polyvinylidene fluoride-trifluorethylene-bromotrifluoroethylene, polyvinylidene fluoride-tetrafluorethylene-bromotrifluoroethylene, 25 polyvinylidene fluoride-tetrafluorethylene-chlorofluoroethylene, polyvinylidene fluoride-trifluorethylene-vinylidene chloride, and polyvinylidene fluoride-tetrafluorethylene-vinylidene chloride.

9. A polymer of claim 1, wherein said polymer exhibits an elastic 30 energy density, at room temperature, of 0.3 joules/cm³ or higher.

10. The polymer of claim 8, wherein said polymer is selected from the group consisting of polyvinylidene fluoride-trifluoroethylene-chlorofluoroethylene P(VDF-TrFE-CFE), polyvinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene P(VDF-TrFE-CTFE),

5 polyvinylidene fluoride-tetrafluoroethylene-chlorotrifluoroethylene, polyvinylidene fluoride-trifluoroethylene-hexafluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-hexafluoroethylene, polyvinylidene fluoride-trifluoroethylene-tetrafluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-tetrafluoroethylene, polyvinylidene fluoride-trifluoroethylene-vinyl fluoride, polyvinylidene fluoride-tetrafluoroethylene-

10 vinyl fluoride, polyvinylidene fluoride-trifluoroethylene-perfluoro(methyl vinyl ether), polyvinylidene fluoride-tetrafluoroethylene-perfluoro(methyl vinyl ether), polyvinylidene fluoride-trifluoroethylene-bromotrifluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-bromotrifluoroethylene,

15 polyvinylidene fluoride-tetrafluoroethylene-chlorofluoroethylene, polyvinylidene fluoride-trifluoroethylene-vinylidene chloride, and polyvinylidene fluoride-tetrafluoroethylene-vinylidene chloride.

11. An electrical or electromechanical device comprising at least

20 one layer of a polymer of claim 1.

12. The electrical or electromechanical device of claim 11, wherein Said polymer is selected from the group consisting of polyvinylidene fluoride-trifluoroethylene-chlorofluoroethylene P(VDF-TrFE-CFE),

25 polyvinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene P(VDF-TrFE-CTFE), polyvinylidene fluoride-tetrafluoroethylene-chlorotrifluoroethylene, polyvinylidene fluoride-trifluoroethylene-hexafluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-hexafluoroethylene, polyvinylidene fluoride-trifluoroethylene-

30 tetrafluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-tetrafluoroethylene, polyvinylidene fluoride-trifluoroethylene-vinyl fluoride,

polyvinylidene fluoride-tetrafluoroethylene-vinyl fluoride, polyvinylidene fluoride-trifluoroethylene-perfluoro(methyl vinyl ether), polyvinylidene fluoride-tetrafluoroethylene-perfluoro(methyl vinyl ether), polyvinylidene fluoride-trifluoroethylene-bromotrifluoroethylene, polyvinylidene fluoride-
5 tetrafluoroethylene-bromotrifluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-chlorofluoroethylene polyvinylidene fluoride-trifluoroethylene-vinylidene chloride, and polyvinylidene fluoride-tetrafluoroethylene-vinylidene chloride.

10 13. A process for the preparation of a polymer comprising:

polymerizing a mixture of three monomers comprising at least one monomer of vinylidene-fluoride; at least one monomer selected from the group consisting of trifluoroethylene and tetrafluoroethylene; and at least
15 one monomer selected from the group consisting of tetrafluoroethylene; vinyl fluoride; perfluoro (methyl vinyl ether); bromotrifluoroethylene; chlorofluoroethylene; chlorotrifluoroethylene; and hexafluoroethylene;

stretching said polymer greater than its original length; and
20 thereafter

annealing said polymer at a temperature below its melting point, wherein said polymer exhibits an electrostrictive strain, at room temperature, of 3% or more when an electric field gradient of 100
25 megavolts per meter or greater is applied thereacross, exhibits a dielectric constant, at room temperature, of 40 or higher at 1 kHz, and exhibits an elastic energy density, at room temperature, of 0.3 joules/cm³ or higher, or any combinations thereof.

30 14. The process of claim 13, wherein said polymer is stretched at least four times its original length.

15. The process of claim 13, wherein said polymer is annealed at a temperature of at least 1 ° F below its melting point, preferably from 1° F to 30°F below its melting point, and more preferably from 5° F to 15 ° F below its melting point.

16. The process of claim 13, wherein said polymer is selected from the group consisting of polyvinylidene fluoride-trifluoroethylene-chlorofluoroethylene P(VDF-TrFE-CFE), polyvinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene P(VDF-TrFE-CTFE), polyvinylidene fluoride-tetrafluoroethylene-chlorotrifluoroethylene, polyvinylidene fluoride-trifluoroethylene-hexafluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-hexafluoroethylene, polyvinylidene fluoride-trifluoroethylene-tetrafluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-tetrafluoroethylene, polyvinylidene fluoride-trifluoroethylene-vinyl fluoride, polyvinylidene fluoride-tetrafluoroethylene-vinyl fluoride, polyvinylidene fluoride-trifluoroethylene-perfluoro(methyl vinyl ether), polyvinylidene fluoride-tetrafluoroethylene-perfluoro(methyl vinyl ether), polyvinylidene fluoride-trifluoroethylene-bromotrifluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-bromotrifluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-chlorofluoroethylene, polyvinylidene fluoride-trifluoroethylene-vinylidene chloride, and polyvinylidene fluoride-tetrafluoroethylene-vinylidene chloride.

17. A polymer prepared by prepared by a polymerizing a mixture of three monomers comprising:

at least one monomer of vinylidene-fluoride;

at least one monomer selected from the group consisting of of trifluoroethylene and tetrafluoroethylene; and

at least one monomer selected from the group consisting of tetrafluoroethylene; vinyl fluoride; perfluoro (methyl vinyl ether); bromotrifluoroethylene; chlorofluoroethylene; chlorotrifluoroethylene; and
 5 hexafluoroethylene, wherein said polymer exhibits an electrostrictive strain, at room temperature, of 3% or more when an electric field gradient of 100 megavolts per meter or greater is applied thereacross, exhibits a dielectric constant, at room temperature, of 40 or higher at 1 kHz, and exhibits an elastic energy density, at room temperature, of 0.3 joules/cm³
 10 or higher, or any combinations thereof.

18. The polymer of claim 17, wherein said polymer is selected from the group consisting of polyvinylidene fluoride-trifluoroethylene-chlorofluoroethylene P(VDF-TrFE-CFE), polyvinylidene fluoride-
 15 trifluoroethylene-chlorotrifluoroethylene P(VDF-TrFE-CTFE), polyvinylidene fluoride-tetrafluoroethylene-chlorotrifluoroethylene, polyvinylidene fluoride-trifluoroethylene-hexafluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-hexafluoroethylene, polyvinylidene fluoride-trifluoroethylene-tetrafluoroethylene, polyvinylidene fluoride-
 20 tetrafluoroethylene-tetrafluoroethylene, polyvinylidene fluoride-trifluoroethylene-vinyl fluoride, polyvinylidene fluoride-tetrafluoroethylene-vinyl fluoride, polyvinylidene fluoride-trifluoroethylene-perfluoro(methyl vinyl ether), polyvinylidene fluoride-tetrafluoroethylene-perfluoro(methyl vinyl ether), polyvinylidene fluoride-trifluoroethylene-bromotrifluoroethylene,
 25 polyvinylidene fluoride-tetrafluoroethylene-bromotrifluoroethylene, polyvinylidene fluoride-tetrafluoroethylene-chlorofluoroethylene, polyvinylidene fluoride-trifluoroethylene-vinylidene chloride, and polyvinylidene fluoride-tetrafluoroethylene-vinylidene chloride.

ABSTRACT

There are disclosed new polymer materials having improved
5 electric field induced strain levels, dielectric constants, and elastic energy
densities for use in electromechanical and dielectric applications.
Methods of manufacture of new polymer materials are also disclosed.

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Fig. 1

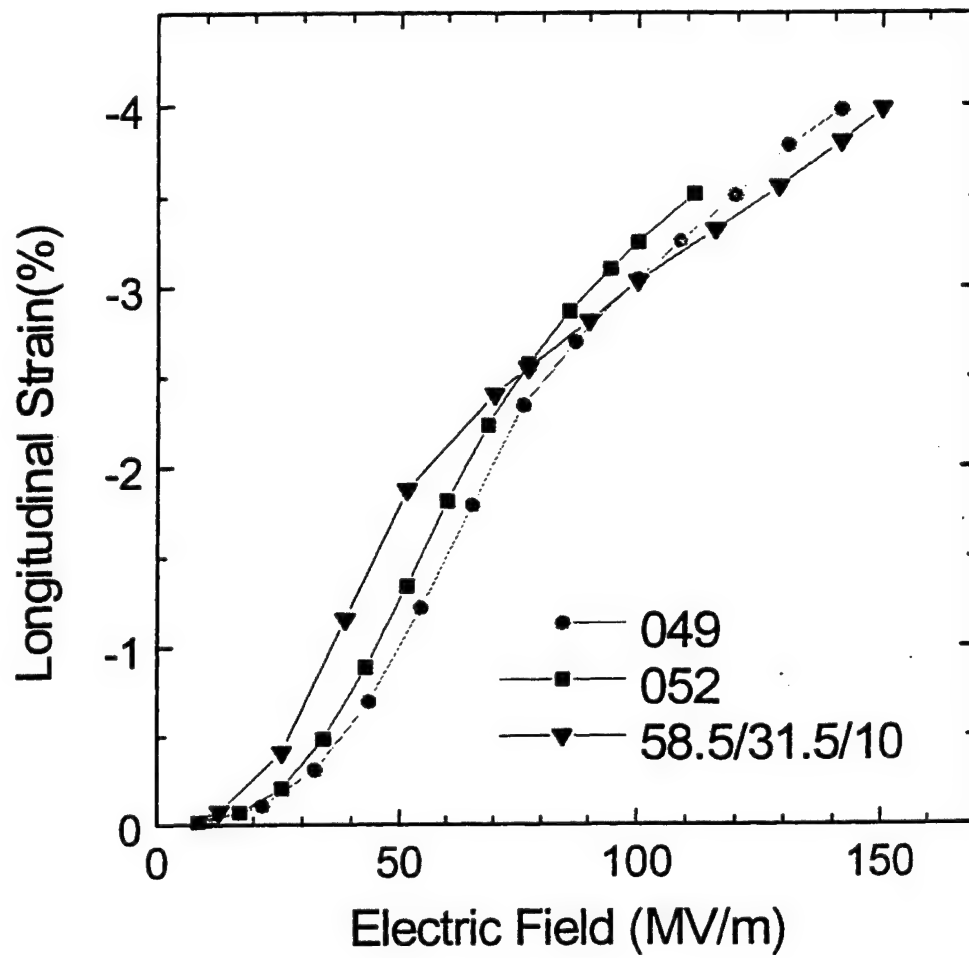


Fig. 2

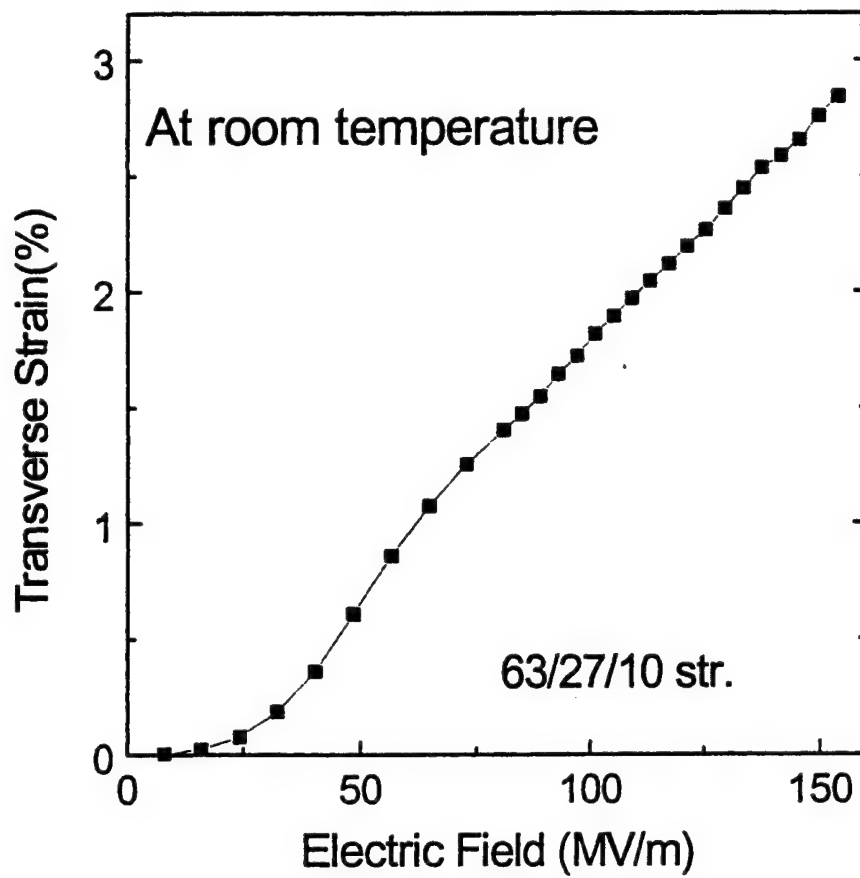


Fig 3

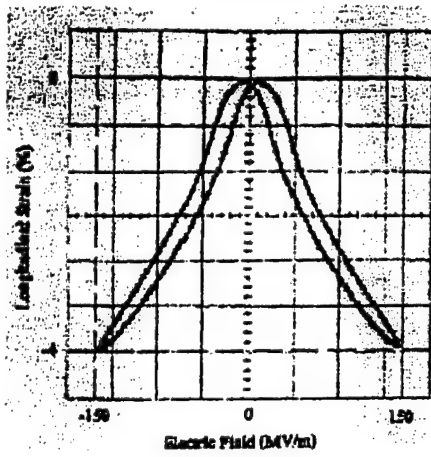


Fig. 4a

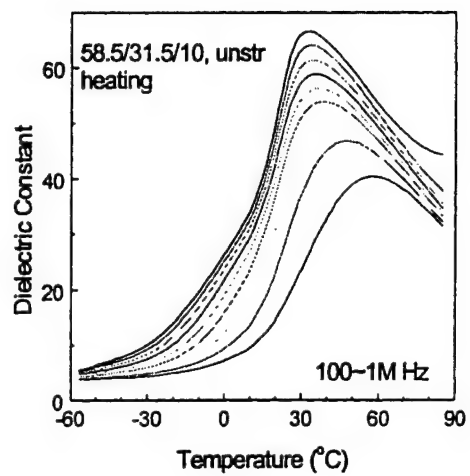


Fig. 4b

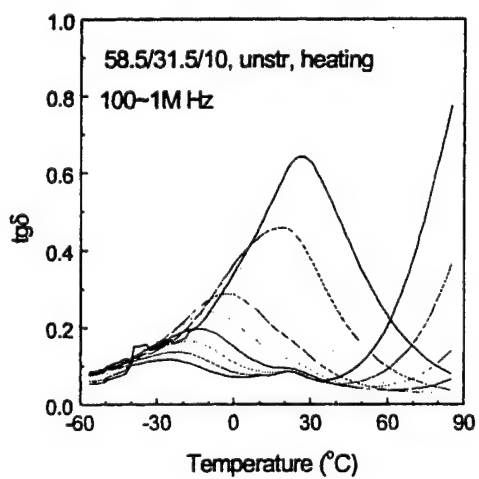
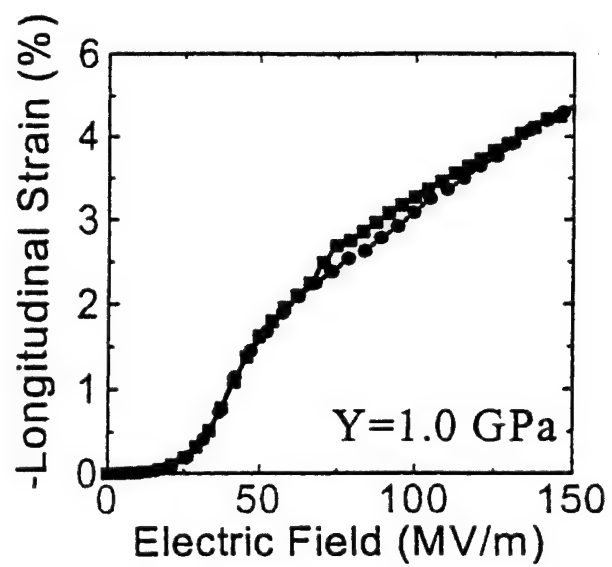


Figure 5



APPENDIX 4

High electrostrictive strain under high mechanical stress in electron-irradiated poly(vinylidene fluoride-trifluoroethylene) copolymer

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In this letter, we show that the electric field induced strain in the electron irradiated poly(vinylidene fluoride-trifluoroethylene) copolymer can generate high strain even under a high mechanical stress. The observed change in strain with stress is due to the electrostrictive coupling of the local polarization with stress, and can be directly related to the change of the induced strain with temperature. The results indicate that the field induced strain observed in the films investigated is indeed from the local polarization regions in the material, and is electrostrictive in nature. © 1999 American Institute of Physics. [S0003-6951(99)03743-2]

Polymers which can generate high electric field induced strain are very attractive for a broad range of applications such as artificial muscles, robots, ultrasonic transducers for medical diagnosis, sonar, and active control of mechanical systems.¹ It was found recently that under a proper electron irradiation treatment, a massive electrostrictive strain can be induced in poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] copolymers. Because of the high elastic modulus of the material, it also possesses a high elastic energy density.²⁻⁵ Being a polymeric material, the electromechanical response under high mechanical load is always a concern, that is, whether the material can maintain the strain level when subject to high external stresses. For example, several polymers such as polyurethane, polybutadiene, silicone rubber etc, were observed to generate very high electric field induced strains up to ~10%.⁶⁻⁹ But due to the fact that these materials have a very low elastic modulus and the strain is caused by the Maxwell stress effect, the elastic energy density of these polymers is low and the strain diminishes even under the mechanical constraints of the metal electrodes deposited on the samples.⁶ In this letter, we demonstrate that the irradiated P(VDF-TrFE) copolymer films can generate a high strain under a high external load. In addition, the experimental results also show that due to the ferroelectric nature of the material, the mechanical load effect on the field induced strain can be directly linked to the variation of the strain with temperature.

The PVDF(x)-TrFE($1-x$) copolymer with $x=65$ mol % was chosen for this study. Among the compositions investigated, this composition showed the highest electrostrictive strain in both the longitudinal and transverse directions (parallel and perpendicular to the applied electric field). The copolymer powder was purchased from Solvay and Cie, Bruxelles, Belgium. The unstretched and uniaxially stretched ($4.5\times$) films of thickness ~20–30 μm were prepared by melt pressing and solution casting methods, respectively. In order to improve the crystallinity and also to remove residual solvent, the films were annealed in a vacuum oven at 140 °C for 16 h. These films were irradiated in a nitrogen atmosphere with 2.55 MeV electrons at 95 °C and with a 60 Mrad dose.

A cantilever based dilatometer was used to measure the

strain along the stretching direction (transverse strain, S_1) at different tensile stresses (σ_T) applied in the same direction.⁴ The strain along the thickness direction (longitudinal strain, S_3) was measured at different hydrostatic pressures (σ_h) using a piezoelectric bimorph based sensor.⁹ In this setup, one end of the piezoelectric bimorph was fixed while the other was in contact with the sample. Under an ac electric field, the expansion and contraction along the sample thickness direction generate the corresponding bending motion in the bimorph sensor. Through the piezoelectric effect, an electrical output voltage which is proportional to the bending of bimorph is observed. Both the setups were designed and developed specifically for strain measurements in polymer films under load. In both cases, the ac electric field is applied along the film thickness with frequencies ranging from 1 to 10 Hz.

Since the magnitude of the transverse strain is higher for stretched films in comparison to unstretched films, the 65/35 stretched films were used to measure the transverse strain at different tensile stresses along the stretching direction. As can be seen from Fig. 1, under a constant electric field, the transverse strain initially increases with the load and reaches to a maximum at the tensile stress of about 20 MPa. Upon further increase of the load, the field induced strain is reduced. One important result revealed by the data is that even under a tensile stress of 45 MPa, the strain generated is still nearly the same as that it was without load, indicating that the material has a very high load capability.

The longitudinal strain for unstretched 65/35 mol % films as a function of hydrostatic pressure was measured and the data is presented in Fig. 2. As can be seen, at low driving electric fields, the strain does not change much with pressure. On the other hand, for high fields it shows increases with pressure. Due to the limitation of the experimental setup, we could not apply pressure higher than 8.2 MPa.

The results from both experiments clearly demonstrate that the electrostrictive P(VDF-TrFE) copolymer has a high load capability and maintains its strain level even under a very high mechanical load, which is in contrast to many other polymeric materials.⁶⁻⁹ However, the increase of the field induced strain with load and the strain maximum observed in Fig. 1 seems to be puzzling. In the following, we

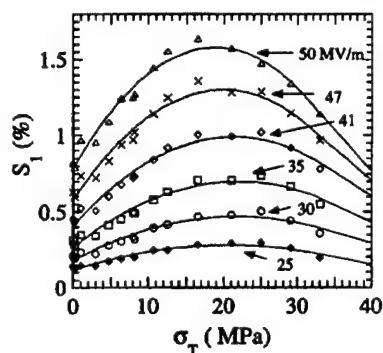


FIG. 1. Effect of tensile stress (σ_T) on electric field induced transverse strain (S_1) measured at room temperature under different driving electric field strengths.

will be showing that the observed phenomena can be understood by considering the electrostrictive coupling of the local polarization with stress in this relaxor ferroelectric material.

It is well known that the unirradiated P(VDF-TrFE) 65/35 mol % copolymer is a normal ferroelectric polymer with a Curie temperature near 70 °C.¹⁰ After the irradiation, we have shown that the material is transformed into a relaxor ferroelectric, which exhibits a large electrostrictive strain.² According to the Landau–Devonshire phenomenological theory, when a normal ferroelectric material is subjected to an external stress, its Curie point will shift, which can be described as^{11,12}

$$\Delta T = 2\epsilon_0 C Q \Delta \sigma, \quad (1)$$

where ΔT is the shift of the Curie temperature, ϵ_0 is permittivity in free space, C is Curie–Weiss constant, σ is the applied stress, and Q is electrostrictive coefficient. Therefore, depending on the sign of the electrostrictive coefficient and the applied stress, the shift of the Curie point can be either positive (to higher temperature) or negative (to lower temperature). For a relaxor ferroelectric, if we use the simple Smolensky model¹³ that a relaxor ferroelectric can be regarded as consisting of local polar regions with different Curie points over a broad temperature range, Eq. (1) can still be used to provide a qualitative understanding of the data.

For the irradiated P(VDF-TrFE) copolymer, it is also shown that the strain is proportional to the square of the induced polarization P :²

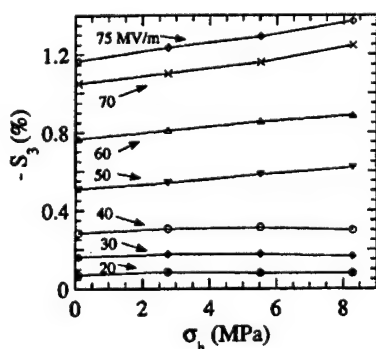


FIG. 2. Effect of hydrostatic pressure (σ_h) on electric field induced longitudinal strain (S_3) measured at room temperature under different driving electric field strengths.

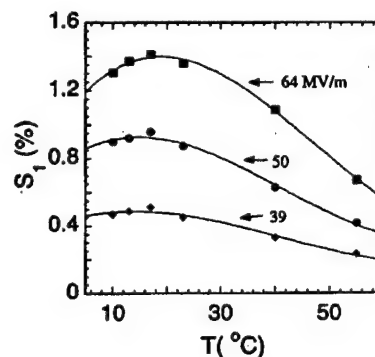


FIG. 3. Variation in electric field induced transverse strain (S_1) as a function of temperature measured under stress free conditions at different electric field strengths.

$$S = QP^2. \quad (2)$$

The relevant electrostrictive coefficients used in Eq. (1) for the irradiated copolymer are: Q_{13} (transverse coefficient, related to the transverse tensile stress) and Q_h (volume coefficient, related to the hydrostatic pressure). From early experimental results, it has been shown that $Q_{13} > 0$ and $Q_h < 0$.⁵ Therefore, under a transverse tensile stress, $\Delta \sigma_T > 0$, and Eq. (1) dictates that the applied tensile stress will shift the Curie temperature downwards. In an analogy, under hydrostatic pressure, $\Delta \sigma_h < 0$, and with increased pressure, the Curie temperature will also move downwards. Combining this with the results in Figs. 1 and 2 suggests that at temperatures near room temperature, both the longitudinal and transverse strains of the samples studied should increase as the temperature is reduced and will reach to a maximum at a temperature below room temperature.

Figures 3 and 4 present the temperature dependence of the transverse strain for the stretched film and the longitudinal strain for the unstretched film measured under stress free conditions at a field range similar to those used in Figs. 1 and 2. Figure 3 shows that for the transverse strain measured in the stretched sample, there is a broad maximum at a temperature near 17 °C in the electric field range measured, which seems to be consistent with the data in Fig. 1. For the longitudinal strain, the temperature limitation of the setup prevents the experiment from being performed below room temperature, and the results in Fig. 4 are consistent with the data in Fig. 2. That is, the field induced strain decreases with

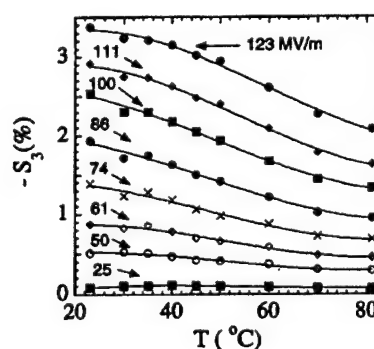


FIG. 4. Variation in electric field induced longitudinal strain (S_3) as a function of temperature measured under stress free condition at different electric field strengths.

temperature. It should be pointed out that due to the nature of relaxor ferroelectric material, the induced strain changes with stress or temperature are also dependent on the level of the driving electric field. For the unstretched sample, the data in Fig. 4 seems to indicate that there is a weak strain maximum at a temperature near 35 °C when the measurement was made under a field of 25 MV/m.

From the data presented in Figs. 1 and 3 for the stretched films and in Figs. 2 and 4 for unstretched films, one may obtain the effective electrostrictive coefficients using Eq. (1) if the Curie-Weiss constants are known for the two samples. Using the Curie-Weiss relation, $\epsilon = C/(T - T_c)$, where ϵ is the permittivity of the material,¹² the values of the Curie-Weiss constants ($C = 4002$ and 3475) and Curie-Weiss temperatures ($T_c = 10.24$ and 28 °C) were calculated for unirradiated stretched and unstretched films, respectively. These values are found to be close to the values reported by others.¹⁰ The value of $Q_{13} = 4.6 \text{ m}^4/\text{C}^2$ is calculated from Eq. (1) using $\Delta T = 6$ °C (Fig. 3) and $\Delta \sigma_T = 18.4 \text{ MPa}$ (Fig. 1), which is very close to the value of $Q_{13} = 4.9 \text{ m}^4/\text{C}^2$ obtained directly from the strain and polarization using Eq. (2).⁵ Although for a system as complicated as the irradiated P(VDF-TrFE) copolymer, we do not expect that the analysis presented can be used quantitatively, the consistency in the effective electrostrictive coefficient obtained from the two sets of data does indicate that the observed change of the induced strain with stress is due to the electrostrictive coupling of the local polarization with stress in this material. For unstretched films, by comparing the slopes from the curves under 75 MV/m in Fig. 2 and under 74 MV/m in Fig. 4, we obtain $Q_h = -10.8 \text{ m}^4/\text{C}^2$ which is also consistent with $Q_h = -6 \text{ m}^4/\text{C}^2$ obtained directly from the measured volume

strain with polarization.⁵ The results obtained here clearly indicate that the field induced strain is due to the local polarization in the material and is electrostrictive in nature. The data presented show that the variation of the field induced strain with stress can be related qualitatively to the change in strain with temperature through Eq. (1) even for a complicated system such as the relaxor ferroelectric P(VDF-TrFE) copolymer. Furthermore, the data show that the electrostrictive strain from the irradiated P(VDF-TrFE) copolymer has a high load capability.

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¹T. T. Wang, J. M. Herbert, and A. M. Glass, *The Application of Ferroelectric Polymers* (Blackie, Chapman and Hall, New York, 1988).

²Q. M. Zhang, V. Bharti, and X. Zhao, *Science* **280**, 2101 (1998).

³V. Bharti, X.-Z. Zhao, and Q. M. Zhang, *Mat. Res. Innovat.* **2**, 57 (1998).

⁴Z.-Y. Cheng, V. Bharti, T.-B. Xu, S. Wang, and Q. M. Zhang, *J. Appl. Phys.* **86**, 2208 (1999).

⁵Z.-Y. Cheng, T.-B. Xu, V. Bharti, S. Wang, and Q. M. Zhang, *Appl. Phys. Lett.* **74**, 1901 (1999).

⁶R. E. Pelrine, R. D. Kornbluh, and J. P. Joseph, *Sens. Actuators A* **64**, 77 (1998).

⁷J. Su, Q. M. Zhang, and R. Y. Ting, *Appl. Phys. Lett.* **71**, 386 (1997).

⁸M. Zhenyi, J. I. Scheinbeim, J. W. Lee, and B. A. Newman, *J. Polym. Sci., Part B: Polym. Phys.* **32**, 2721 (1994).

⁹J. Su, P. Moses, and Q. M. Zhang, *Rev. Sci. Instrum.* **69**, 2480 (1998).

¹⁰T. Furukawa, *Phase Transit.* **18**, 143 (1989).

¹¹M. E. Lines and A. M. Glass, *Principal and Applications of Ferroelectrics and Related Materials* (Oxford University Press, New York, 1977).

¹²A. F. Devonshire, *Philos. Mag.* **3**, 85 (1954).

¹³G. A. Smolensky, *J. Phys. Soc. Jpn.* **28**, 26 (1970).

APPENDIX 5

Electromechanical Behavior of Electroactive P(VDF-TrFE) Copolymers

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ABSTRACT

An exceptionally high electrostrictive response was observed in electron irradiate polyvinylidene fluoride-trifluoroethylene (P(VDF-TrFE)) copolymer. Moreover, the transverse strain of the material can be tuned over a large range by different sample treatment conditions. For example, in films uniaxially stretched, the strain can be comparable or even larger than the longitudinal strain, while in films unstretched, the transverse strain is quite small. In addition, when the films are completely clamped mechanically in the lateral directions, the films can still generate large longitudinal strains. Due to relatively high elastic modulus of the films, high elastic strain energy densities, which are much higher than those in conventional piezo and electrostrictive ceramics and magnetostrictive materials.

Keywords: Actuator materials, electrostriction, P(VDF-TrFE), Ferroelectrics

1. INTRODUCTION

Materials which generate large mechanical actuation induced by external stimuli have attracted a great deal of attention in recent years. The advance of smart materials and structures challenges the materials society to develop materials with high strain levels, low hysteresis, relatively fast response and high strain energy density. Although there are many active materials currently available, there are few that meet those requirements. For instance, piezoceramic and magnetostrictive materials, while possessing low hysteresis and fast response, suffer low strain level.^{1,2} On the other hand, shape-memory alloys generate high strain but are often associated with large hysteresis and slow response.³ In this paper, we report the finding of an exceptionally high electric field induced strain with low hysteresis (electrostrictive) response from electron irradiated P(VDF-TrFE) copolymers. Furthermore, we will present experimental evidence showing that the polymer also possesses a large elastic strain energy density, a feature important for most of smart materials and structures applications.

The P(VDF-TrFE) copolymer was from Solvay & Cie of Belgium. The film used in this investigation was fabricated by either melt press or solvent (DMF) cast methods. The film thickness was between 25 m and 40 m. Two types of films were used in the investigation, unstretched and stretched films. Unstretched films were directly annealed at 140 °C in a vacuum for 12 hours to improve the crystallinity. As will be shown, although a large longitudinal strain can be achieved in unstretched films these films show a relatively low transverse strain. The stretched films were prepared by uniaxially stretching the film at a temperature between 25 – 50 °C with a stretching ratio of 5 times. The films after stretching were also annealed in vacuum at 140 °C for 12 hours. The irradiation treatment was carried out in a nitrogen atmosphere with 3 MeV electrons and the dosage was in the range between 40 Mrad and 100 Mrad. The electrodes were made by gold sputtering on the polymer films.

In this investigation, the electric field induced longitudinal strain was characterized by a bimorph based strain sensor designed specifically for the polymer film strain measurement.⁴ The transverse strain was measured by a set-up with a cantilever beam and a photonic sensor which was also used to evaluate the load effect on the transverse strain responses. The polarization hysteresis loop was measured by a Sawyer-Tower circuit. The elastic compliance was measured by a Dynamic Mechanical Analyzer in the frequency range from 1 to 200 Hz.

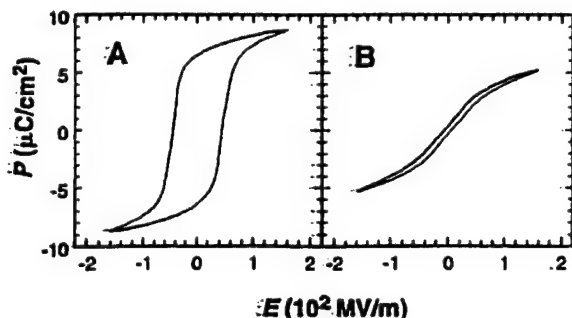


Figure 1.

The polarization hysteresis loops of P(VDF-TrFE) 50/50 copolymer measured at room temperature.

- (a) Before irradiation;
- (b) After irradiation with 40 Mrad dosage at 120 °C.

2. POLARIZATION AND LONGITUDINAL STRAIN RESPONSES

Presented in figure 1(a) is the polarization hysteresis loop for P(VDF-TrFE) 50/50 film measured at room temperature before the electron irradiation. As expected, the material exhibits a well defined ferroelectric polarization loop with a coercive field at 45 MV/m and a remanent polarization of 6.4 C/cm². In contrast, the sample irradiated with 40 Mrad dosage at 120 °C exhibits a slim hysteresis loop and the polarization level of the sample is also reduced (figure 1(b)). Similar result was also obtained for samples irradiated at room temperature with 80 Mrad electron dosage. The result here is consistent with the early finding by Lovinger that electron irradiation of P(VDF-TrFE) can destroy the ferroelectricity in the material.⁵

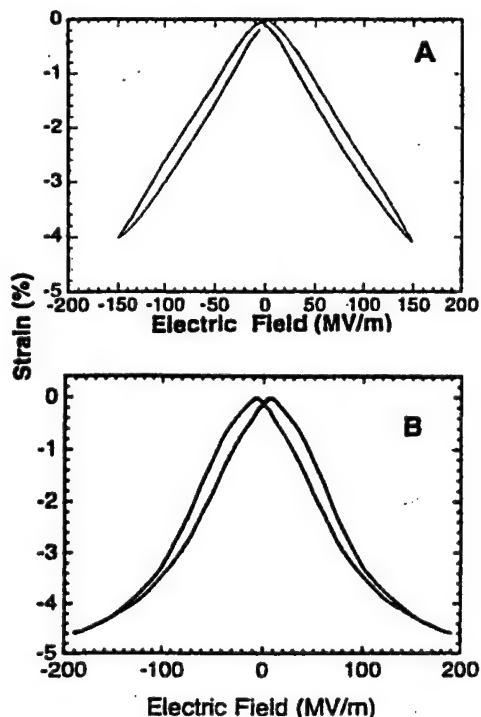


Figure 2.

- (a) The strain-field dependence of P(VDF-TrFE) 50/50 copolymer after irradiation with 40 Mrad dosage at 120 °C.

- (b) 65/35 stretched and irradiated with 40 Mrad dose at 120 °C.

Most interestingly, the films after the irradiation show a high strain response as presented in figures 2(a) and 2(b) for films of P(VDF-trFE) 50/50 irradiated at 120 C with 40 Mrad and P(VDF-TrFE) 65/35 stretched and irradiated at room temperature with 80 Mrad dose. Apparently, the results demonstrate that an exceptionally high electric field induced strain with little hysteresis can be achieved in this class of materials.

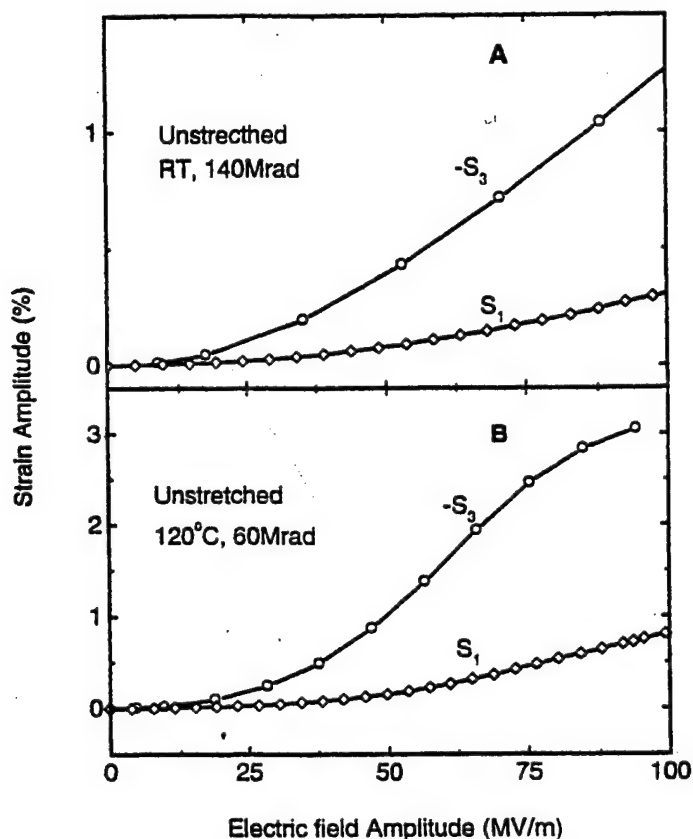


Figure 3. The amplitude of electriective longitudinal (S_1) and transverse strain (S_3) as a function of the applied field. The films were irradiated at room temperature with 140 Mrad dose and at 120°C with 60 Mrad dose, respectively. The data points are shown in the figure and the solid cures are drawn to guide eyes.

Table 1. Comparison of Strain and Strain Energy Density

Materials		Y (GPa)	S_m (%)	$YS_m^2/2(J/cm^3)$	$YS_m^2/2p$
P(VDF-TrFE) Electrostrictor	S_L	0.4	4.5	0.4	200
	S_T	1.3	3.0	0.59	294
Piezoceramic		64	0.2	0.13	17
Magneto-strictor		100	0.2	0.2	21.6
PZN-PT Single Crystal		7.7	1.7	1.0	131

Clearly, materials with such high electrostrictive strain is attractive for actuator, sensor, and transducer applications. However, in very soft polymers the Maxwell stress effect, originated from the Coulomb force of the charges, can deform

material. Both the volumetric energy density which is proportional to $Y S_m^2/2$ and related to the device volume, and the gravimetric energy density which is proportional to $Y S_m^2/2$ and related to the device weight are included in the comparison, where Y is the elastic modulus, S_m is the strain level, and ρ is the density of the material, respectively.⁷ In Table I, we compare the newly discovered P(VDF-TrFE) copolymer with several current known materials, including the ferroelectric relaxor single crystal PZN-PT, which was discovered recently to possess an ultrahigh strain response.⁸ Apparently, the electrostrictive P(VDF-TrFE) copolymer discovered here exhibits a significantly improved performance.

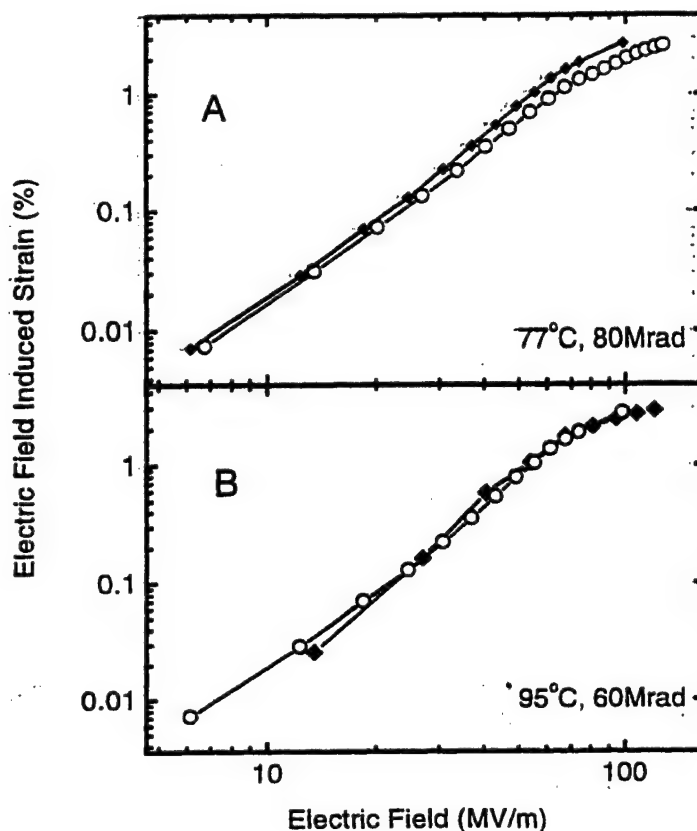


Figure 4. Comparison between the transverse strain along the stretching direction (S_1 , shown as circle in the figure) and the longitudinal strain (S_3 , shown as diamond in the figure) for stretched films. The solid curves are drawn to guide eyes.

3. TRANSVERSE STRAIN RESPONSES

One of the interesting features of this newly discovered material is that its transverse strain can be tuned over a large range. Shown in figure 3 are the transverse and longitudinal strains of two unstretched films of 65/35 composition, one irradiated with 140 Mrad dose at room temperature and the other with 60 Mrad dose at 120°C. The strain response is electrostrictive and the data in figure 3 is plotted as the amplitude of induced strain versus the amplitude of applied field. One interesting feature of figure 3 is that in spite of a large difference in the strain levels between the two films, the ratio of $|S_1/S_3|$ is nearly the same for both films (at 0.25). For most of the unstretched films examined, this ratio is in the range from 0.25 to 0.33 which is smaller than those in the conventional piezoceramics where the ratio is at about 0.4 or higher.⁹ For P(VDF-TrFE) copolymers, it is well known that a change in polarization will result in a strain along the polymer chain direction in opposite sign to that perpendicular to the chain direction. It is this cancellation effect of these two strains that produces a

small transverse strain in unstretched films. From the data in figure 3(b), the volume strain for the copolymer film irradiated at 120 °C with 60 Mrad can be determined: $S_v = -1.5\%$ under a field of 100 MV/m which is about half of the longitudinal strain.

In contrast to the results in figure 3, the stretched films of P(VDF-TrFE) 65/35 mol% exhibit a much higher transverse strain response when measured along the stretching direction and the results are presented in figure 4 where the data is presented as the amplitude of induced strain versus the amplitude of applied field. At 100 MV/m driving field, the transverse strain S_1 can reach 2.7% for films irradiated at 95 °C with 60 Mrad dose. At higher dosages, the strain is reduced, while at lower dosages, strain hysteresis was observed. The comparison between S_2 and S_1 is made in figure 4 and for the two films shown in the figure, the ratio of $|S_1/S_2|$ is 1.03 for the film in figure 4(b) (60 Mrad dose irradiated at 95 °C) and 0.8 for the film in figure 4(a) (80 Mrad dose irradiated at 77 °C). Hence, the stretched films can have a transverse strain which magnitude approaches that of the longitudinal strain. It is well known that uniaxial stretching of P(VDF-TrFE) copolymer films aligns the polymer chains along the drawing direction which enhances the strain response in that direction.¹⁰

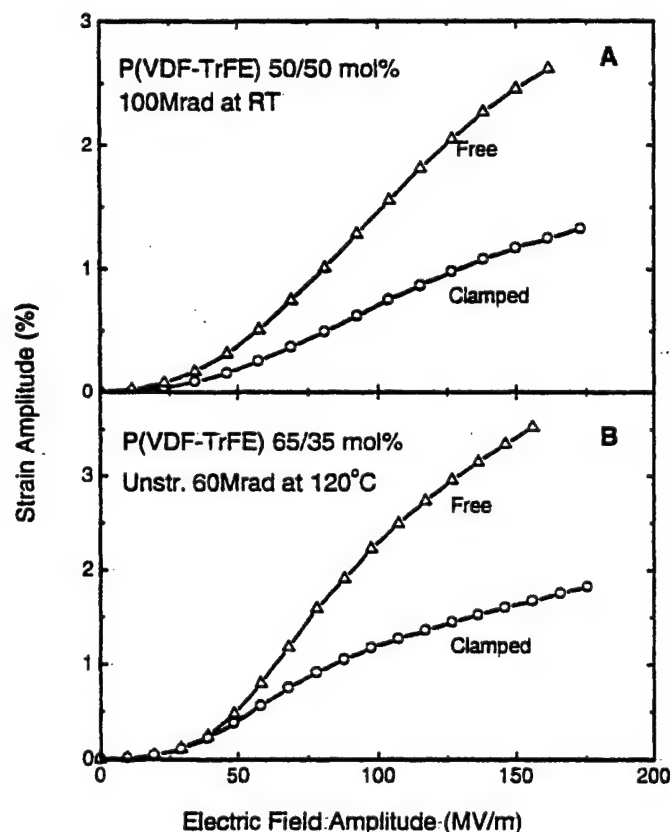


Figure 5. (A) Comparison of the longitudinal strains without lateral clamping (free) and with lateral clamping (Clamped) for 50/50 mol% films irradiated with 100 Mrad at temperature; (B) Comparison of the longitudinal strains without lateral clamping (free) and with lateral clamping (clamped) for 65/35 mol% films irradiated with 60 Mrad at 120°C.

4. LONGITUDINAL STRAIN RESPONSES IN Laterally CLAMPED POLYMER FILMS

For polymer electroactive materials, one of the concerns is how the longitudinal strain will change when the sample is mechanically clamped laterally. For strains induced by Maxwell stress effect in isotropic polymers, a lateral clamping can reduce the longitudinal strain to nearly zero. Hence, the longitudinal strain responses were also measured for unstretched films which were clued to a thick solid substrate (several mm thick brass plates). The transverse strain of the films is zero due to the mechanical clamping from the substrate. Shown in figure 5(a) is the comparison of the

longitudinal strain for 50/50 composition irradiated at room temperature with 100 Mrad. The strain after the clamping is still near 50 % of that without clamping. While for 65/35 copolymer, as shown in figure 5(b), the strain after clamping is more than 50% of the original strain (no clamping). Therefore, the polymer can still deliver a high strain response even when it is constrained severely in the lateral direction. This is consistent with the large volume strain observed in these polymer films. Results will also be reported in the future that the electrostrictive polymers developed here have a high load ability as consistent with the high elastic strain energy density listed in table I.

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REFERENCES

1. L. E. Cross, *Ceram. Trans.* **68**, 15 (1996).
2. K. B. Hathaway and Arthur E. Clark, "Magnetostrictive Materials", *MRS Bulletin*, **18**, 34 (1993).
3. S. M. Wayman, "Shape memory alloys", *MRS Bulletin*, **18**, 49 (1993).
4. J. Su, P. Moses, and Q. M. Zhang, "A bimorph based dilatometer for field induced strain measurement in soft and thin free standing polymer films", *Rev. Sci. Instruments*, **69**, 2480 (1998).
5. A. J. Lovinger, "Polymorphic Transformations in Ferroelectric copolymers of Vinylidene Fluoride Induced by electron Irradiation", *Macromolecules*, **18**, 910 (1985).
6. Q. M. Zhang, J. Su, C. Kim, R. Ting, and R. Capps, "An experimental investigation of electromechanical responses in a polyurethane elastomer", *J. Appl. Phys.* **81**, 2770 (1997).
7. V. Giurgiutiu, Z. Chaudhry, and C. Rogers, "Energy-based Comparison of Solid-State Actuators," *Report No. CIMSS 95-101*, Virginia Polytechnic Institute and State University, 1995.
8. Seung-Eek Park and T. Shrout, "Ultrahigh strain and piezoelectric behavior in relaxor based ferroelectric single crystals", *J. Appl. Phys.* **82**, 1804 (1997).
9. B. Jeffe, W. Cook, H. Jeffe, "*Piezoelectric Ceramics*", Academic Press, OH, 1971.
10. T. Furukawa, "Ferroelectric Properties of Vinylidene Fluoride copolymers", *Phase Transition*, **18**, 143 (1989).

APPENDIX 6

High performance of all-polymer electrostrictive systems

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ABSTRACT

All-polymer electrostrictive systems are developed. Two typical electro-active polymers, poly(vinylidene-trifluoroethylene) P(VDF-TrFE) of high elastic modulus and polyurethane of low elastic modulus, are studied. The conducting polymers used as electrodes in the system are polypyrrole and polyaniline respectively. The compatible interface between the electrode polymer and electrostrictive polymer produces acoustic transparency of the all-polymer films. The dielectric and electromechanical properties of the system are characterized and compared with that of the electroactive polymer with gold electrodes. It is found that the dielectric loss of the system is a little bit higher than that of the sample with gold electrodes at high frequency since the conductivity of the conductive polymer is lower than that of the gold. The electric field induced longitudinal strain response of the all-polymer system is the same as that of the electroactive polymer with gold electrodes. However, the electric field induced transverse strain response of the all-polymer system is higher than that of the electroactive polymer with gold electrodes.

Keywords: Electrostriction, Polypyrrole, Polyaniline, Poly(vinylidene-trifluoroethylene), Conductive Polymer, Actuator, Transducer

1. INTRODUCTION

Electroactive materials have been the primary source of actuation materials for smart structures and drive mechanisms.¹ Numerous applications have been reported including ultrasonic and undersea sonic techniques, robotics, vibration isolation, and manipulation. The basic behavior of the material used in these applications is the strain response induced by electric field or others. So far, most of electroactive materials used in the applications are electroactive ceramics. However, recently it is found that the polymers, such as polyurethane and electron irradiated poly(vinylidene-trifluoroethylene) (P(VDF-TrFE)) copolymer, can exhibit very large electric field induced strain response.^{2,3,4} Especially, P(VDF-TrFE) copolymer is of relative large elastic modulus. The electron irradiated P(VDF-TrFE) exhibits the highest elastic energy in all of the electroactive materials even considering the ceramics and single crystal of inorganic materials.² These attract a great deal of attention. These electroactive polymers have important potential applications in transducer, sensor, and actuator technologies.⁵ The advantage of the polymer over ceramics is its flexibility, low acoustic impedance, and others. However, in order to use these useful properties, the electrode material is an important issue; since the conventionally-used metal electrodes, such as Au, Ag and Al, have high acoustic impedance and impose mechanical clamping on the soft polymer which can significantly reduce the electromechanical efficiency of the electromechanical transducer the polymer made. Considering the high conductivity, low acoustic impedance, and the flexibility of the conducting polymers, it is very interesting to use the conducting polymers as the electrodes for the electromechanical transducer the electroactive polymer made. Thus, the all-polymer electroactive system was proposed recently by us.⁶ In an all-polymer electroactive system, the conducting polymer is used as the electrodes to replace the conventionally-used metal electrodes. Due to its flexibility, strong coherent interfaces, and significantly improved acoustic transparency, such an all-polymer electrostrictive system may improve the performance of electromechanical polymer materials in acoustic applications.

In this paper, the performance of the so-called all-polymer system is reported. Considering the processability and conductivity, two typical conducting polymers, polypyrrole (PPY) and polyaniline (PANI), are studied in this work. The

electroactive polymers used here are polyurethane and P(VDF-TrFE) copolymer. Both electroactive polymers are electrostrictive. Thus, the system studied here can be called the all-polymer electrostrictive system.

2. EXPERIMENTS

2.1 Sample Preparation

Polyurethane films of various thicknesses were produced by a solution casting method followed by a 100 °C annealing for 30 minutes as described in the earlier publication.⁷ P(VDF-TrFE) copolymer films with different ratio of vinylidene were fabricated by melt-pressing powders at 225 °C. The films were annealed at 120 °C for 24 hrs. The thickness of the films studied here was in the range from 30 to 60 μm . The electron irradiation was carried out at different temperatures with different dosages under nitrogen atmosphere using the electron energy of 3MeV. The details of the process for fabricating P(VDF-TrFE) films are discussed in our earlier publications.^{2,8}

The conducting PPY electrodes were deposited on both surfaces of the films by an in-situ deposition technique. In the procedure, freshly distilled pyrrole was dissolved in distilled water. The pyrrole solution was then poured into another aqueous solution containing proper amounts of ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and doping agents to form a polymerizing solution. The prepared electroactive polymer (polyurethane or P(VDF-TrFE)) films were immersed into the polymerizing solution and allowed to undergo the in-situ deposition of conducting PPY on both surfaces of the films under ambient laboratory conditions. In order to obtain PPY electrodes with desirable quality and thickness, the polymer films were removed from the polymerizing solution and rinsed with distilled water for ~ 10 seconds several times during the deposition process. The resultant PPY electrodes were smooth and coherent to the polymer films. The surface electric resistivity measured with a four probe method was about $1000\Omega/\square$ for the PPY electrode with a thickness about 300Å.

The conducting PANI electrodes were fabricated by coating the PANI solution in m-cresol on both surfaces of the electroactive polymer films. Then, the films with PANI solution were dried at 50 °C in hood for 10 minutes to evaporate the solvent. The conductivity of PANI prepared here is about 250 S/cm. With regard to the preparation of PANI solution, PANI in salt form was prepared by chemical oxidation of aniline with ammonium persulphates oxidant in 1.5M HCl solution at about 0 °C, according to the reference.⁹ Emeraldine base form (EB) of PANI was obtained by treating the salt form with 3% NH_4OH for 2h. The EB powder was mixed with HCSA in the molar ratio of 0.5 HCSA per repeat unit of PANI. The mixture was ground under nitrogen atmosphere to a fine powder and then dissolved in m-cresol. The solution was treated in an ultrasonic bath and subsequently, centrifuges. Minor insoluble solids were removed by decanting.¹⁰

In order to prepare the electrodes with special patterns, circle or tetragon, a metal mask was used in both PPY and PANI cases. In addition, in order to compare the performance of an all-polymer electrostrictive system with that of electroactive polymer with metal electrodes, the gold electrodes of 400Å were also sputtered on both surfaces of the electroactive polymer films.

2.2 Measurements

The dielectric properties of the electrostrictive system at room temperature were measured by HP 4274A, HP 4284A and HP 4192A respectively in different frequency ranges. The temperature dependence of the dielectric behavior was measured through a DEA 2870 Dielectric Analyzer (TA Instruments Co.) with a heating or cooling rate of 2 °C/minute. The polarization hysteresis loops were measured by a Sawyer Tower circuit at the frequency of 1 Hz and 10 Hz with a different electric field.

The electric induced strain response of the films was measured at room temperature along both longitudinal and transverse direction. The longitudinal strain, the strain along the external electric field direction, was measured through a piezoelectric bimorph based dilatometer at frequencies from 1 Hz to 100 Hz.¹⁰ The detail discussion of the set-up and its applications can be found in the earlier publications. The transverse strain, the strain along the direction perpendicular to the external electric field direction, was measured through a cantilever based dilatometer at frequencies from 0.01 Hz to 10 Hz. The details of the set-up are presented in reference 11.

3. RESULTS AND DISCUSSION

3.1 Frequency Dependence of Dielectric Properties

The frequency dependence of the capacitance and loss of an electrostrictive film, unstretched P(VDF-TrFE) 65/35 mol% film electron irradiated at room temperature with 140 Mrad dosage in nitrogen gas atmosphere, is shown in Fig. 1. Where the samples of the same thickness with PPY and gold electrode, respectively, were measured at room temperature. From Fig. 1, one can find at high frequency that the dielectric loss of the sample with PPY electrodes is higher than that with gold electrodes.

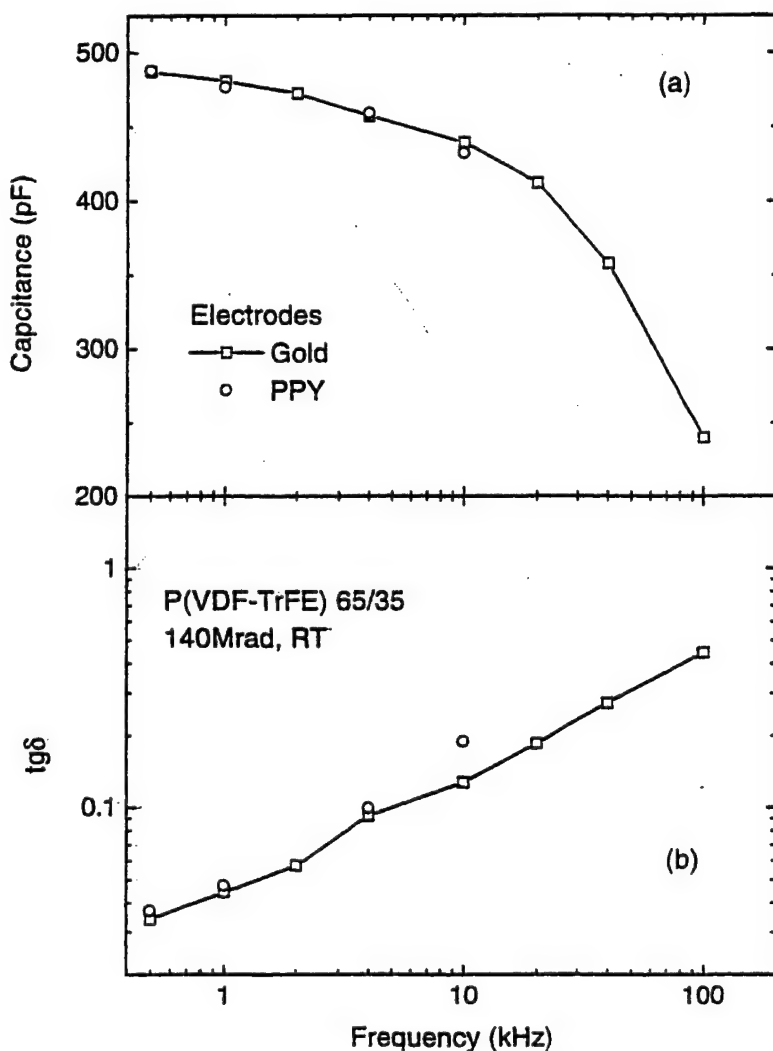


Fig. 1. The frequency dependence of the capacitance (a) and dielectric loss (b) of an unstretched P(VDF-TrFE) 65/35 mol% copolymer film irradiated at room temperature with 140 Mrad dosage in nitrogen gas atmosphere. The dielectric behavior of the film was measured with PPY and gold electrodes, respectively. The samples with PPY and gold electrodes have the same thickness and the electrode area.

It is found that the dielectric loss of the sample with conducting polymer electrodes is always a little bit higher than that with gold electrodes. However, the difference of the dielectric loss between the sample with conducting polymer electrodes and the sample with gold electrodes is strongly dependent on the parameters of the conducting polymer electrode, such as the thickness and conductivity. The other result is shown in Fig. 2, where PANI electrodes were used. The sample was an electrostrictive film, P(VDF-TrFE) 50/50 mol% film electron irradiated at 120 °C with 30Mrad dosage.

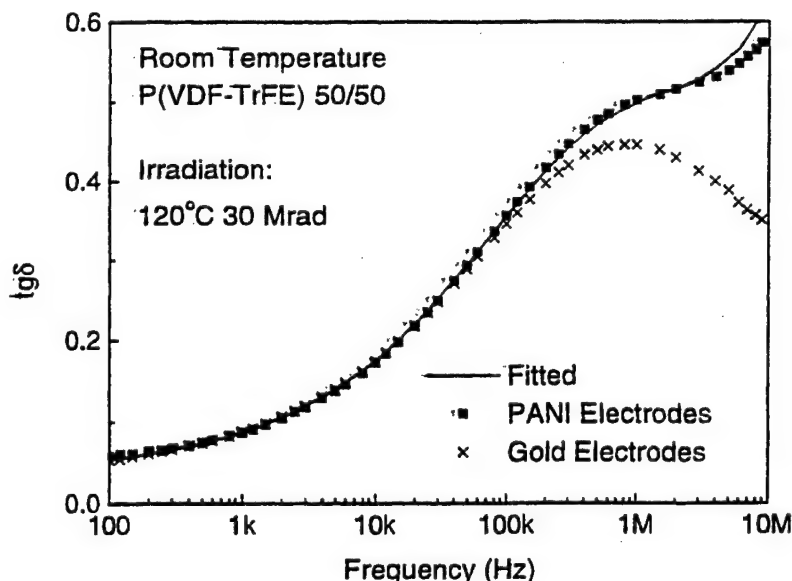


Fig. 2 The frequency dependence of the dielectric loss of an electrostrictive film, P(VDF-TrFE) 50/50 film electron irradiated at 120 °C with 30 Mrad dosage in nitrogen gas atmosphere. The samples with PANI and gold electrodes, respectively, were measured at room temperature. The solid line is the fitted results.

In order to find the reason, the dielectric properties of the sample with gold electrodes are assumed as the real properties of the material, while the dielectric properties of the sample with conducting polymer electrodes are thought as the material serialized with a resistance. With only this one parameter (resistance), the dielectric properties of the sample with conducting polymer electrodes are estimated from the dielectric properties of the material. The estimated results are plotted as a solid line in Fig. 2. Clearly, the fitted results are very close to the measured results. From the fitting, it is found that at the same frequency the higher the resistance of the conducting polymer electrodes is, the higher the measured dielectric loss of the sample. While for the same resistance of the conducting polymer electrodes, the higher the frequency is, the more difference is obtained. All these indicate that the difference of the dielectric properties for the samples with different electrodes mainly originates from the influence of the electrode's resistance. That is, the conducting polymer does not change the physical properties of the material studied. Moreover, the results indicate that one can get the sample with conducting polymer electrodes for special application in the different frequency range through changing the parameters (thickness and conductivity) of the conducting polymer.

3.2 Temperature Dependence of Dielectric Properties

The other concern about the conducting polymer electrodes is the working temperature range. This is an important issue since the actuators are generally used in a relatively broad temperature range. Clearly, the working temperature range of the conducting polymer electrodes is limited by the decomposition temperature of the conducting polymer, which is generally very high compared to the decomposition temperature of electroactive polymer materials, and the loss of the doping effect, which is related to the conducting polymer molecular and the doping molecular.

The temperature dependence of the dielectric constant and dielectric loss at 100 Hz of the polyurethane film with the PPY electrodes is shown in Fig. 3. The results from the polyurethane film with gold electrodes is also shown in Fig. 3. From Fig. 3, one can find that at temperatures lower than about 35 °C the samples with different electrodes exhibit similar dielectric

properties. This is consistent with above investigations of the frequency dependence of the dielectric properties of the samples with different electrodes at room temperature. This again indicates that the direct deposition process of PPY does not change the physical properties of the electroactive polymers present studied.

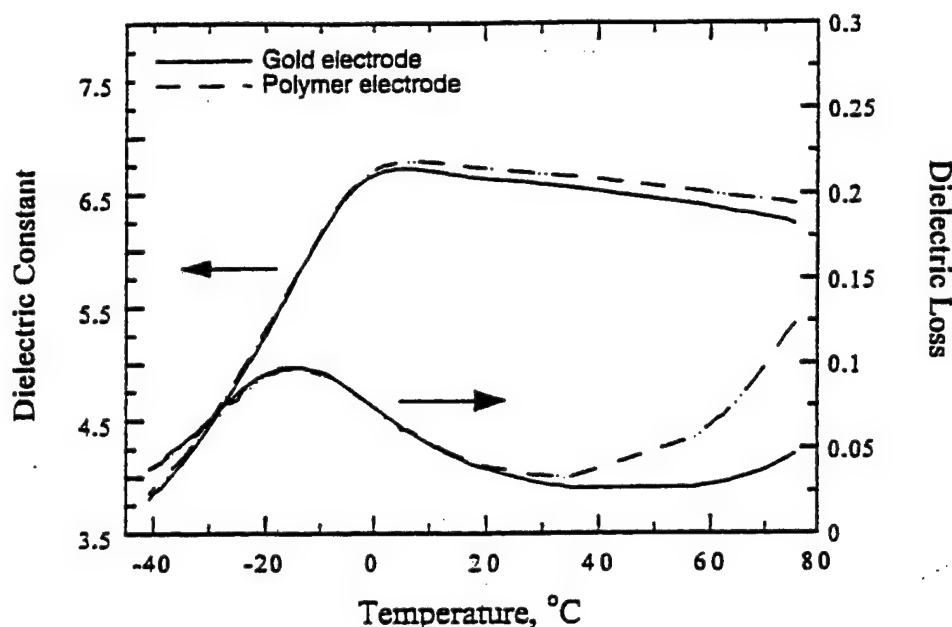


Fig. 3 Temperature dependence of the dielectric constant and dielectric loss at 100 Hz of polyurethane with PPY and gold electrodes, respectively.

Anyhow, at temperatures higher than 40 °C, the results in Fig. 3 indicate that the dielectric loss of the sample with PPY electrodes is clearly higher than that with gold electrodes. This marked increase of the dielectric loss of the sample with PPY electrodes might be a consequence of dehydration phenomena in the conducting PPY, which has been suggested by several researchers and should occur in the temperature range from 60 °C to 100 °C.^{13,14}

With regard to PANI electrodes, the temperature dependence of the dielectric constant and dielectric loss at 30 kHz for P(VDF-TrFE) 65/35 mol% copolymer film irradiated at 120 °C with 30 Mrad dosage is shown in Fig. 4. Again, in the low temperature range (lower than about 100 °C here), the samples with different electrodes exhibit similar dielectric properties. However, at a high temperature range (higher than about 120 °C), clear difference on the dielectric properties was obtained for the samples with different electrodes. The difference might be a consequence of deprotonation of the PANI gradually, which has been suggested by the other researchers and starts at a temperature around 100 °C.¹⁵

The results in Fig. 4 and Fig. 3 indicate that the conductive PANI/HCSA electrodes are better than PPY. In addition, the fabrication process of PANI electrodes is simple and uses little time. All these indicate the advantage of PANI/HCSA used as the electrodes in all-polymer electroactive system. However, it should be noticed that the above study of PANI electrodes was only performed on electron irradiated P(VDF-TrFE) copolymer films and that the PANI solution in m-cresol was used. Since the crosslinking happened during the irradiation, m-cresol did not make any change in the irradiated P(VDF-TrFE) copolymer film when the solution was dried quickly. However, for the other electroactive polymer, m-cresol might result in some changes in the electroactive polymer. Thus, in order to utilize the advantage of the PANI in all-polymer electroactive system, a hydro-based solution of PANI is expected.

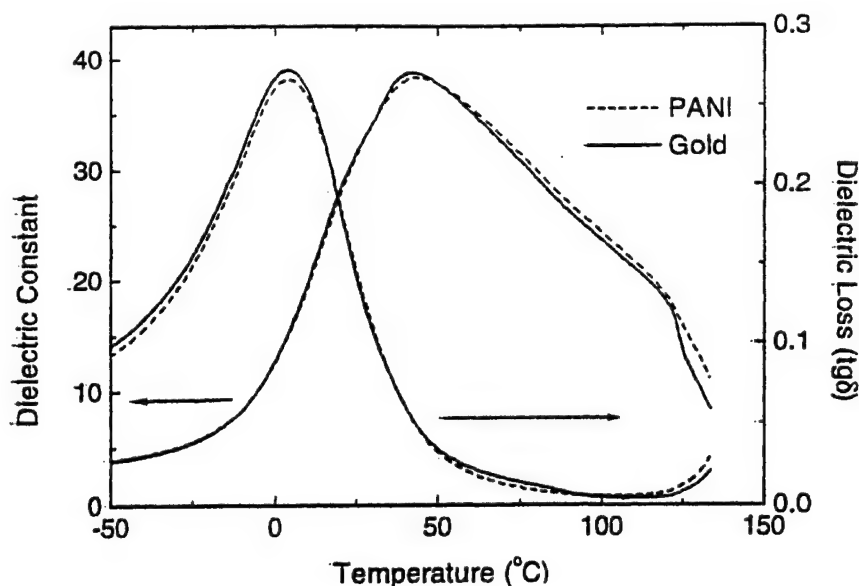


Fig. 4 Temperature dependence of the dielectric constant and dielectric loss at 30 kHz of P(VDF-TrFE) 65/35 mol% copolymer film (electron irradiated at 95 °C with 60 Mrad dosage in nitrogen atmosphere) with PANI and gold, respectively.

3.3 Polarization Hysteresis Loop

It should be noticed that all of the above studies of the dielectric behavior of the all-polymer electrostrictive system were performed at weak external electric field. However, in order to obtain large electric field induced strain response on the electrostrictive polymer, a high electric field is needed to drive the polarization. Thus, it is very interesting to know the dielectric behavior of the all-polymer system at a high electric field.

The polarization behavior of the above all-polymer electrostrictive system at room temperature was measured in the frequency range from 0.1 Hz to 10 Hz. The external electric field applied on the all-polymer system is from nearly zero to about 150 MV/m. The polarization behavior of the same electroactive polymer with gold electrodes was also measured under the same conditions. The results indicate that the polarization behavior of the all-polymer system at strong electric field is also similar to that of the electroactive polymer with gold electrodes. This indicates that the conducting polymer studied here (PPY and PANI) can function well as the electrodes on the electrostrictive polymer.

3.4 Electric Field Induced Strain

In order to directly characterize the performance of the all-polymer electrostrictive systems developed above, the electric field induced strain response of the system was measured.

With regard to the electric field induced longitudinal strain response, two kinds of experiments were performed. First of all, the experiments were performed at a constant frequency. It is found that the strain response of the all-polymer system can be a little bit smaller/higher than that of the same electroactive polymer film with gold electrodes, sometimes. In any case, the difference of the strain response between the two kinds of the samples is small. That is, there was no clear relation of the longitudinal strain response to the two kinds of samples. Second, the frequency dependence of the strain response for the sample at a constant electric field was measured. It is found that there are some differences between the two kinds of the samples. However, the difference is not much. It was found that the space charge has some contributions to the measured longitudinal strain of electrostrictive polymers.¹⁶ Both the amount and distribution of the space charge in the material have the effect on the longitudinal strain response. Clearly, the amount and distribution of the space charge in the polymer depend on the process, how to prepare the electrodes and material used as the electrodes. That is, the space charge in the

polymer can result in the difference on the longitudinal strain response for the same electrostrictive film with different electrodes or preparing process. All these indicate that the longitudinal strain response of the all-polymer system is nearly the same as that of the electroactive polymer film with gold electrodes.

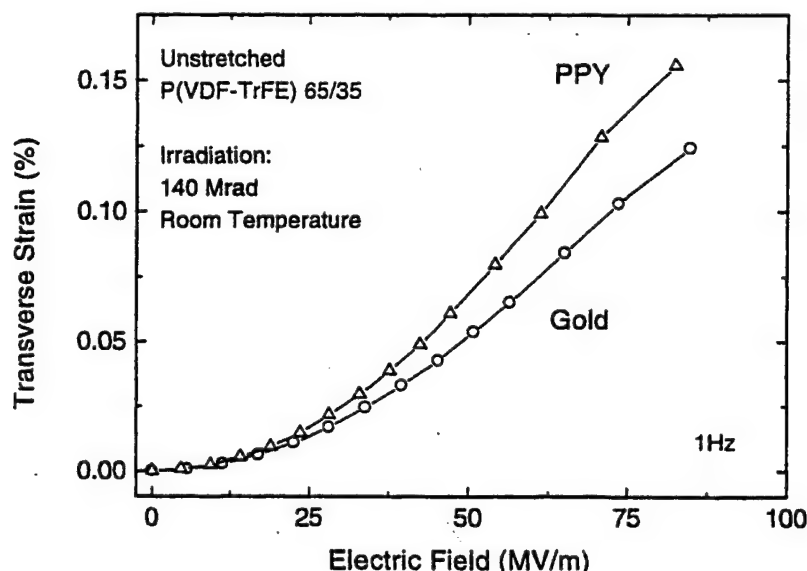


Fig. 5 Transverse strain response of unstretched P(VDF-TrFE) 65/35 film under different electric field of 1Hz with both PPY and gold electrodes respectively. The film was irradiated at 135 °C with 140 Mrad dosage.

Besides the longitudinal strain response, the transverse strain response of the electroactive material has many applications, such as the bimorph, unimorph. The transverse strain response of unstretched P(VDF-TrFE) 65/35 mol% film irradiated at 135 °C with 140 Mrad dosage, which exhibits a relatively high longitudinal strain response in all examined P(VDF-TrFE) copolymer films was measured using PPY and gold as electrodes, respectively. The results are shown in Fig. 5. The data in Fig. 5 clearly shows that the performance of the all-polymer system is much better than that with gold electrodes. It is known that the transverse strain response of unstretched P(VDF-TrFE) electrostrictive film is much smaller than the longitudinal strain response of the same film. However, the transverse strain response of stretched P(VDF-TrFE) electrostrictive film can be as high as the longitudinal strain.¹⁷ Thus, it is more interesting to see the performance of the all-polymer electrostrictive system in the case with a large transverse strain. The results of a stretched P(VDF-TrFE) 65/35 electrostrictive film irradiated at 95 °C with 60 Mrad dosage, which exhibits the largest transverse strain response for all the examined P(VDF-TrFE) copolymer films at the electric field lower than 100 MV/m, are shown in Fig. 6. Clearly, the transverse strain response of the stretched film is much higher than that of the unstretched one. The data in Fig. 6 indicates again that the performance of the all-polymer electrostrictive system is much better than that of the electrostrictive film with gold electrodes.

In order to understand the different influence of the conducting polymer electrodes on the longitudinal and transverse strain responses, respectively, it is better to compare the difference between the conducting polymer and gold. Although the elastic modulus of the sputtered gold electrodes might be smaller than that of the bulk gold, it is believed that the elastic modulus of the sputtered gold electrode is still much higher than that of the conducting polymer electrode. Under external electric field, both conducting polymer and gold do not exhibit any strain response, while the electroactive polymer will exhibit both longitudinal and transverse strain responses. Thus, there are some stresses on the interface between the electroactive polymer film and the electrodes. These stresses are clearly along the transverse direction. These stresses have the different influence on the different strain responses. For the transverse strain response, these stresses have a direct clamping effect on the electroactive polymer. Thus, the more the stress is, the smaller the transverse strain response of the system is. The different transverse strain responses of two kinds of samples indicate that the gold electrodes have a stronger clamping

effect on the electroactive polymer than the conducting polymer electrodes. However, the influence of these stresses on the longitudinal strain response is not direct. Thus, the clamping effect on the longitudinal direction is not clear. That is why the measured longitudinal strain response from the all-polymer system is nearly the same as that from the electroactive polymer with gold electrodes, although the clamping effect of gold electrode is stronger than that of conducting polymer electrodes.

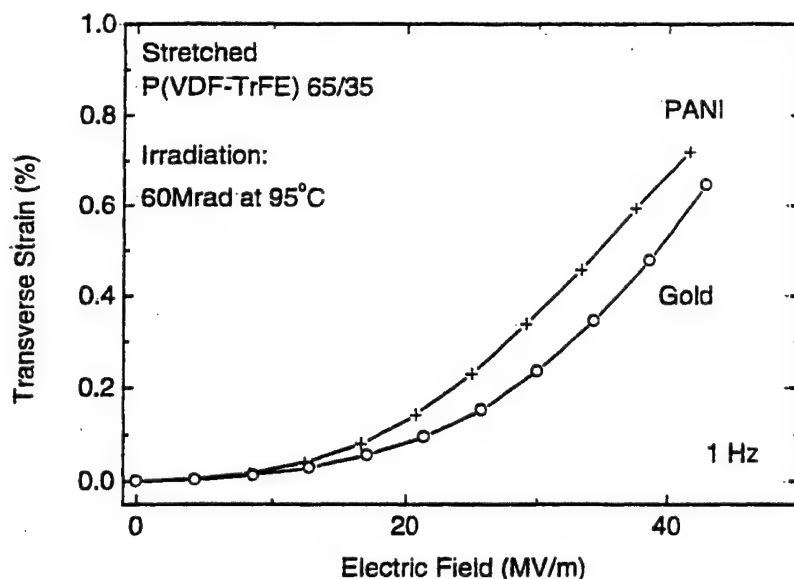


Fig. 6 Transverse strain response vs. electric field of 1 Hz for a stretched electrostrictive film, P(VDF-TrFE) 65/35 mol% irradiated at 95 °C with 60 Mrad dosage. The samples with PANI and gold electrodes were measured, respectively.

4. SUMMARY

All-polymer electrostrictive system systems are fabricated using polyurethane and electron irradiated P(VDF-TrFE) copolymer with PPY and PANI electrodes, respectively. The dielectric study on the system shows that the conducting polymer electrodes did not change the sample. The longitudinal strain response of the all-polymer system is nearly the same as that with gold electrodes. However, the transverse strain response of the all-polymer electrostrictive system is much better than that with gold electrodes. Considering the acoustic impedance of the conducting polymer is nearly the same as that of the electrostrictive polymer, the same or higher electric field induced strain responses of the all-polymer system indicate that a high performance actuator and transducer, especially for applications in regard to human-beings and water, can be obtained with the all-polymer electrostrictive system.

ACKNOWLEDGMENTS

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REFERENCES

1. J.M. Herbert, *Ferroelectric Transducers and sensors*, Gordon and Breach Science Publishers, New York, 1982.
2. Q.M. Zhang, V. Bharti, X. Zhao, "Giant Electrostriction and Relaxor Ferroelectric Behavior in Electron-Irradiated Poly(vinylidene fluoride-trifluoroethylene) Copolymer", *Science*, **280**, 2101(1998).
3. M. Zhenyi, J. I. Scheinbeim, J. W. Lee, and B. A. Newman, "High Field Electrostrictive Response of Polymers", *J. Polym. Sci. Part B: Polym. Phys.*, **32**, 2721 (1994).
4. X. Zhao, V. Bharti, Q. M. Zhang, T. Romotowski, F. Toto, and R. Ting, "Electromechanical Properties of Electrostrictive Poly(vinylidene fluoride-trifluoroethylene) Copolymers", *Appl. Phys. Lett.* **73**, 2054 (1998).

APPENDIX 7

Giant Electrostrictive Response in Poly(Vinylidene Fluoride-Hexafluoropropylene) Copolymers

Xiaoyan Lu, Adriana Schirokauer, and Jerry Scheinbeim

Abstract—Electrostrictive strains were measured in three different polymeric materials: a low modulus polyurethane elastomer, previously studied by Scheinbeim *et al.* [1], and two higher modulus random copolymers of poly(vinylidene fluoride-hexafluoropropylene) [P(VDF-HFP)] with 5% and 15% HFP content. Measurements at increasing voltage (electric fields ranging from 0 to 60 MV/m) were taken using an air gap capacitance system and then converted to sample thickness. Copolymer samples with different thermal histories were compared, ice water quenched, air quenched, and slow cooled, for both compositions. The ice water-quenched 5% P(VDF-HFP) copolymer exhibited the highest strain response ($>4\%$) with a dielectric constant of 13.9. The previously studied polyurethane elastomer exhibited the second highest strain response, $>3\%$, with the lowest dielectric constant, 8.5. The ice water-quenched 15% HFP copolymer exhibited the lowest strain response among the three polymeric materials tested, $\approx 3\%$, with a dielectric constant of 12.2. The strain energy density of the 5% HFP ice water-quenched copolymer, $\frac{1}{2} Y S_m^2$ ($\frac{1}{2}$ Young's modulus, Y , times the maximum electrostrictive strain, S_{max} squared), is the largest known for any semi-crystalline polymer: 0.88J/cm^3 .

I. INTRODUCTION

FIELD-INDUCED electrostrictive strains can be observed in a material upon application of an electric field. These strains are proportional to the square of the applied field. If the strains are large enough, materials with this property offer great promise in applications such as sensors, actuators, artificial muscles, robotics, and MEMS.

Giant electrostrictive strains were first observed in a polyurethane elastomer [1]. The polyurethane exhibited strains $>3\%$ under electric fields of up to 40 MV/m and an elastic modulus on the order of 0.01 GPa. Recently, strains up to 4% were observed in a copolymer of PVDF, poly(vinylidene-fluoride-trifluoroethylene) [P(VDF-TrFE)], upon application of electric fields up to 150 MV/m. These films were subjected to a two-step process in which the materials were first melt-pressed and slow cooled and then irradiated with a high energy electron beam [2]. The irradiated P(VDF-TrFE) films were observed to have an elastic modulus of approximately 0.4 GPa.

In the present study, the strain response of a new class of copolymers of PVDF is investigated. Electrostrictive

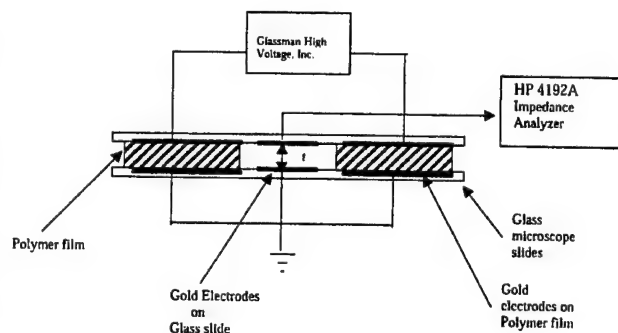


Fig. 1. Schematic diagram of air-gap capacitor system. Air gap electrode area is 4.0 cm^2 .

strains were measured in P(VDF-HFP) random copolymers under electric fields up to 60 MV/m and compared with the response observed in the previously studied low modulus polyurethane thermoplastic elastomer, which is known to have a structure consisting of "hard" crystalline regions holding the "soft" amorphous matrix together [1]. The measurements were taken after the material was melt-pressed and ice water quenched, air quenched, or slow cooled. No further thermal treatment to the films was performed.

II. EXPERIMENTAL

Melt-pressed samples of the copolymers of P(VDF-HFP) were prepared in a Carver Laboratory Press®. The copolymers were obtained as pellets from Soltex and converted into powder in a Spex® Freezer Mill. The powder was then melted at 190°C in the press at 4000 psi. For each composition, three different thermal treatments were used: ice water quenching, air quenching, and slow cooling. The polyurethane films (PU) were provided by Deerfield Urethane, Inc. (Dow 2103-80AE) and were extruded films. All samples were 50 to $60\text{ }\mu\text{m}$ in thickness and were cut into strips of $3 \times 2\text{ cm}$. Two strips of the same film were cut for each kind of sample. Gold electrodes (30 nm in thickness) were deposited on opposing sides of the films using a Sputter Coater [EMS 650®]. One electrode was connected to the high voltage supply, and the other electrode was grounded. The electrode area was $2.5 \times 1.5\text{ cm}$. Electrostrictive strains were measured, using an air gap capacitor (Fig. 1), as a function of electric field up to 60

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MV/m. The capacitance of the air gap, measured using an HP 4192A Impedance Analyzer®, was then related to the strain change in the film. The measured capacitance is related to the air gap thickness through (1):

$$t = \epsilon \cdot A/C \quad (1)$$

where ϵ is the permittivity of air, A is the electrode area, and C is the measured capacitance. Given the arrangement of the polymer films sandwiched between the capacitor plates, the air gap thickness is approximated as the film thickness, t . The percent strain of the film is then approximated to the percent change of the thickness of the air gap. Calibration of the system was first performed using a 1.00-pF standard capacitor. The precision of the measurement was 2%. The accuracy of the capacitance system was also confirmed using the previously tested Deerfield polyurethane films. The results obtained with this system matched the ones previously obtained [1]. For a given composition, the response of ice water-quenched, air-quenched and slow-cooled samples were compared. The elastic modulus and relative dielectric constant were measured as a function of temperature (ranging from -80°C to 100°C) at 100 Hz. The dielectric constant was also measured as a function of frequency (0.01 to 10 kHz) at room temperature. These measurements were performed using a Rheolograph Solid® (Toyoseiki, Japan).

X-ray diffraction patterns were obtained using a Diffraktometer Kristalloflex® Siemens. Values of remanent polarization and coercive field were obtained by poling the films using a Trek® high voltage source Model 610C and Keithley® 617 electrometer and 195A digital multimeter, and the aid of computer software.

III. RESULTS AND DISCUSSION

Both P(VDF-HFP) copolymers of 5 and 15% HFP compositions exhibited similar behavior with respect to thermal treatment; slow-cooled and air-quenched samples showed the smallest response (strains $\approx 1\%$), whereas the ice water-quenched samples exhibited the largest response in both the 5 and 15% HFP compositions. Strains $>4\%$ were observed in the 5% HFP ice water-quenched P(VDF-HFP) copolymer, the largest response observed among all of the samples. This means that the energy density, $YS_{max}^2/2$, is $0.88\text{J}/\text{cm}^3$, the largest for any existing polymer. Following the same behavior, the polyurethane and the 15% HFP ice water-quenched films showed strains $>3\%$. The curves for the 5 and 15% copolymers and the polyurethane film are shown in Fig. 2. The strain response in the polyurethane was only measured up to electric fields of 35 MV/m because of the lower dielectric strength of this material as compared with the copolymers that could withstand much higher electric fields. Values of elastic modulus were lower for the quenched films than for the slow-cooled ones and, in both cases, were higher than the previously studied polyurethane elastomers. The dielectric constants and moduli of the samples measured at 100 Hz

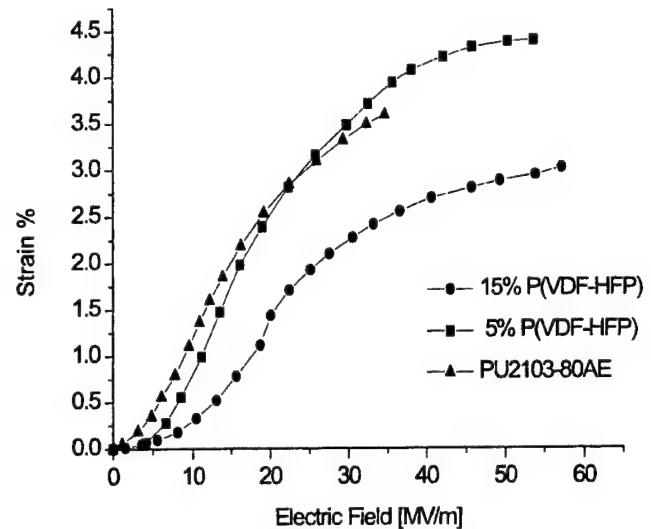


Fig. 2. Strain response of ice water-quenched P(VDF-HFP) 5%, polyurethane and P(VDF-HFP) 15% copolymer as a function of applied electric field.

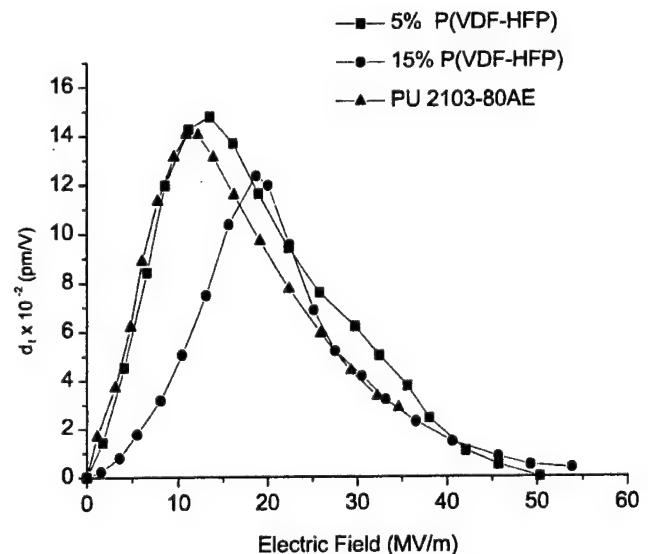


Fig. 3. Thickness coefficient, d_t , as a function of electric field for the two copolymers and the polyurethane.

and room temperature are listed in Table I. The thickness strain constant, d_t , values, i.e., the slope of the strain vs. E curve, are shown in Fig. 3 and indicate the regions of highest thickness response ($d_t = dS/dE$). The thickness strain coefficient, d_t , for the 5% HFP ice water-quenched copolymer was $1700\text{ pm}/\text{V}$. This value of d_t is the highest among all of the samples tested in this work, and it is much higher than the reported value for the PVDF homopolymer, the P(VDF-TrFE) copolymer, and PZT ceramics [3], [4] and higher than the lead magnesium niobate-lead titanate (PMN-PT) system that was reported to have a d_{33} of $1300\text{ pm}/\text{V}$ [6]. Also, this value of d_t is much higher

TABLE I
ELASTIC MODULUS, Y (GPa); DIELECTRIC CONSTANT, ϵ_r ; AND ENERGY DENSITY,
 $YS_{max}^2/2(\text{J}/\text{cm}^3)$, FOR THE TWO COPOLYMERS AND THE
POLYURETHANE BEFORE APPLICATION OF FIELD IN FIG. 2.

Material	Y (GPa)	ϵ_r	$YS_{max}^2/2(\text{J}/\text{cm}^3)$
Ice water-quenched PVDF/HFP, 5%	1.10	13.5	0.88
Ice water-quenched PVDF/HFP, 15%	0.50	12.7	0.29
Polyurethane	0.068	8.5	0.054

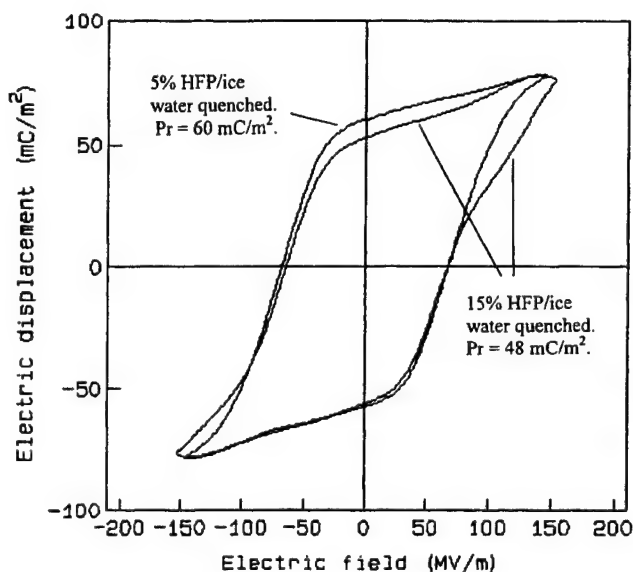


Fig. 4. electric displacement, D , as a function of electric field for both 5 and 15% HFP ice water-quenched copolymers. The remanent polarization values, P_r , are $60 \text{ mC}/\text{m}^2$ for the 5% HFP copolymer and $48 \text{ mC}/\text{m}^2$ for the 15% HFP copolymer.

than that of softer materials, such as the previously studied polyurethane ($d_t \approx 500 \text{ pm}/\text{V}$) and previously studied rubber materials with $d_t \approx 10 \text{ pm}/\text{V}$ [7]. Values of remanent polarization for the 5 and 15% HFP copolymers are shown in Fig. 4. Only the ice water-quenched samples exhibited a D-E hysteresis loop and a remanent polarization. For the 5% HFP ice water-quenched copolymer, the observed remanent polarization is $60 \text{ mC}/\text{m}^2$, and, for the 15% HFP ice water-quenched copolymer, the observed remanent polarization is $48 \text{ mC}/\text{m}^2$. Temperature and frequency scans are shown in Fig. 5 and 6, respectively. The 5% HFP ice water-quenched copolymer shows higher dielectric constant than the 15% HFP ice water-quenched copolymer in the temperature range studied. The frequency behavior is similar for both copolymers. At room temperature and measurement frequency of 104 Hz, the dielectric constant for the 5% HFP ice water-quenched copolymer was 13.9, which is higher than the value reported for the PVDF homopolymer (≈ 12.9) [8] and the value observed in the P(VDF-TrFE) copolymer (≈ 10.4) [3]. The elastic modulus for the 5% HFP ice water-quenched copolymer at room temperature is the highest one of the samples tested, and it is higher than

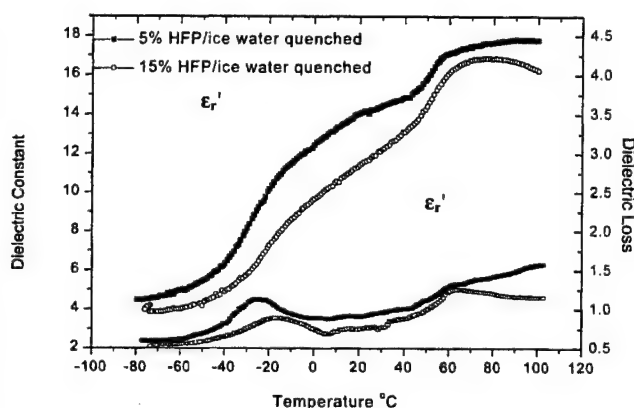


Fig. 5. Dielectric constant as a function of temperature for 5 and 15% HFP ice water-quenched copolymers. The real part is represented by ϵ_r' and the imaginary part by ϵ_r'' . The frequency of the measurements is 104 Hz.

the electron beam irradiated P(VDF-TrFE) copolymer (0.38 GPa). This value is lower than the reported PVDF and nonirradiated P(VDF-TrFE) values [3], which have lower strain response.

X-ray diffraction studies were performed to investigate crystallinity and crystal structures in the copolymer films. As can be seen in the wide angle diffractometer scans (WAXD) in Fig. 7, the slow-cooled samples exhibited the highest crystallinity and the highest modulus; the ice water-quenched samples exhibited the lowest crystallinity and the lowest modulus. The slow-cooled samples were α -form, also seen in the X-ray diffraction scans of the PVDF homopolymer [5], showing the distinct 100, 020, and 110 reflections. The 100 reflection is significantly weaker in the 15% HFP copolymer than in the 5% HFP copolymer as is the 110 reflection. In the ice water-quenched samples, one can only see a combined 100-020 broad peak along with a very broad 110 peak.

IV. CONCLUSIONS

Further research to investigate other structure-property relationships in these copolymers is needed and should be directed toward gaining an understanding of the molecular mechanisms responsible for the observed electrostrictive response.

This work establishes the fact that there exists a range of new materials that, when used in an electrostrictive

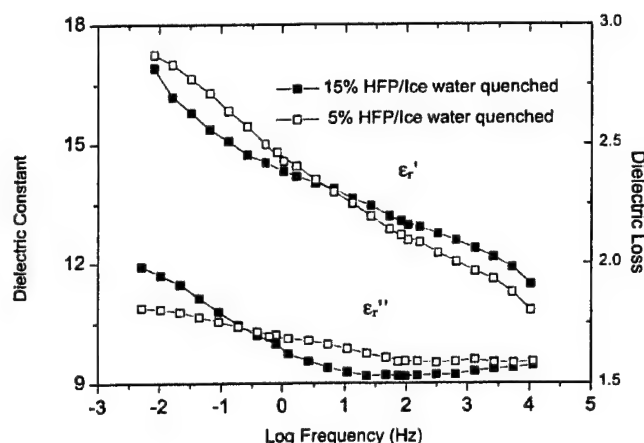


Fig. 6. Dielectric constant as a function of frequency for 5 and 15% HFP ice water-quenched copolymers measured at 20 °C. The real part is represented by ϵ'_r and the imaginary part by ϵ''_r .

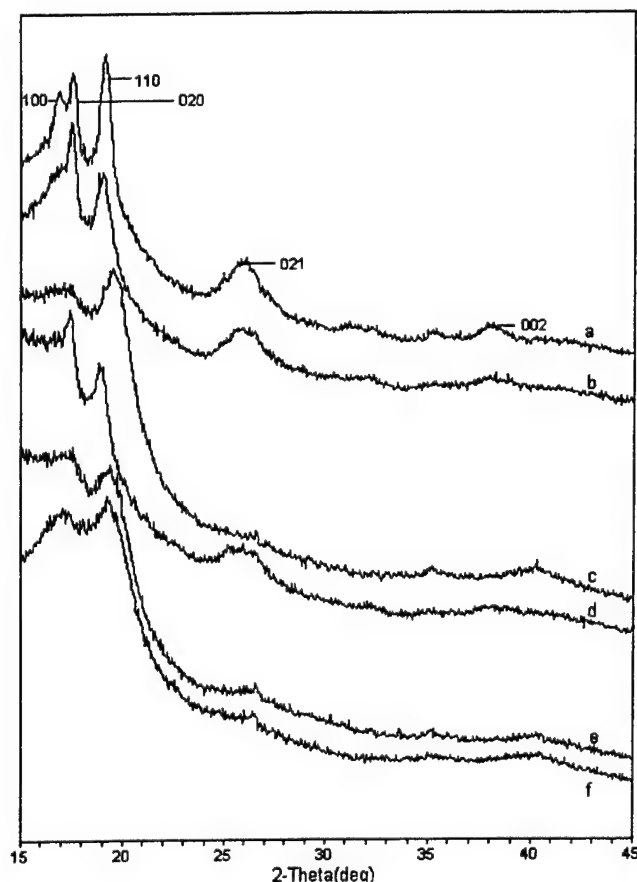


Fig. 7. X-ray diffraction patterns for a) slow-cooled P(VDF/HFP) 5%; b) slow-cooled P(VDF/HFP) 15%; c) air-quenched P(VDF/HFP) 5%; d) air-quenched P(VDF/HFP) 15%; e) ice water-quenched P(VDF/HFP) 5%; and f) ice water-quenched P(VDF/HFP) 15%.

tive mode, can produce extremely large strains with a wide range of energy densities. These include the soft polyurethanes [1]; random copolymers of P(VDF-TrFE), as shown by Zhang *et al.* [2]; and P(VDF-HFP).

REFERENCES

- [1] Z. Ma, J. Scheinbeim, J. Lee, and B. Newman, "High field electrostrictive response of polymers," *J. Polym. Sci.: Part B: Polym. Phys.*, vol. 32, pp. 2721-2731, 1994.
- [2] Q. M. Zhang, V. Bharti, and X. Zhao, "Giant electrostriction and relaxor ferroelectric behavior in electron-irradiated poly(vinylidene fluoride-trifluoroethylene) copolymer," *Science*, vol. 280, pp. 2101-2104, 1998.
- [3] T. Furukawa and N. Seo, "Electrostriction as the origin of piezoelectricity in ferroelectric polymers," *Jpn. J. Appl. Phys.*, vol. 29, no. 4, p. 675, 1990.
- [4] H. Schewe, "Piezoelectricity of uniaxially oriented polyvinylidene fluoride," in *Proc. 1982 Ultrason. Symp.*, B. R. McAvoy, Ed. New York: IEEE, pp. 519-524.
- [5] B. Newman and J. Scheinbeim, "Polarization mechanisms in phase II poly(vinylidene fluoride) films," *Macromolecules*, vol. 16, pp. 60-68, 1983.
- [6] V. Sundar and R. E. Newnham, "Electrostriction and polarization," *Ferroelectrics*, vol. 135, pp. 431-446, 1992.
- [7] Y. Ma and D. H. Reneker, "Electrostriction of rubber sheets," *Proc. Fall ACS Rubber Division Mtg.*, Cleveland, OH, 1996, pp. 674-685.
- [8] Y. Wada and R. Hayakawa, "A model theory of piezo and pyroelectricity of poly(vinylidene fluoride) electret," *Ferroelectrics*, vol. 32, pp. 115-118, 1980.



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Jerry Scheinbeim was born in New York City on August 8, 1942. He received the B.S. degree in physics from Polytechnic Institute of Brooklyn in 1968. He received his M.S. degree in physics from the University of Pittsburgh (1969) and the Ph.D. degree in X-ray crystallography and chemical physics from the University of Pittsburgh (1975). After graduation, he did postdoctoral studies in the Department of Macromolecular Science at Case Western Reserve University for two years. In 1977, he joined the Material Science Department at Rutgers University and is now a full professor. His current research interests are in polymer electroprocessing and structure-property relationships in electroactive polymeric materials. Several

important discoveries and patents of his include the direct oriented crystallization from solution of a ferroelectric polymer under high electric fields; the discovery of the second known class of ferroelectric polymers, the odd and odd-odd numbered nylons; the creation of a new type of composite ferroelectric material, a bilaminate, made from the two known classes of ferroelectric polymers (polyvinylidene fluoride and nylon 11); interfacial effects and the large enhancement in piezoelectric response; and the discovery of the enormous electrostrictive response available in certain polymers.

Dr. Scheinbeim is a member of the American Chemistry Society, American Physical Society, and American Institute of Chemical Engineering.

APPENDIX 8

Effect of High Energy Electron Irradiation on the Electromechanical Properties of Poly(vinylidene Fluoride-Trifluoroethylene) 50/50 and 65/35 Copolymers

Zhong-Yang Cheng, Vivek Bharti, Tian Mai, Tian-Bing Xu, *Member, IEEE*,
Qiming M. Zhang, *Senior Member, IEEE*, Thomas Ramotowski, Kenneth A. Wright, and Robert Ting

Abstract—High energy electron irradiation with a broad range dosage was carried out on poly(vinylidene fluoride-trifluoroethylene) copolymer 65/35 mol% and 50/50 mol% films at different temperatures from room temperature to a temperature close to the melt temperature. The effect of irradiation on the properties of the films, such as electric field-induced strain, dielectric and polarization behaviors, and mechanical modulus, is presented. The irradiated films can exhibit a very large electric field-induced strain, more than 4.5% longitudinal strain, and 3% transverse strain. The transverse strain of the stretched film can compare with the longitudinal strain; that of the unstretched film is much smaller than the longitudinal strain. With regard to the dielectric and polarization behaviors, we found that irradiation changes the copolymer from a typical ferroelectric to a relaxor ferroelectric in which the behavior of microregions under the electric field plays the key role. Between the two copolymers studied, we found that 65/35 copolymer is preferred for both longitudinal and transverse strain generation. A model is proposed to explain the experimental results that the amplitude of the charge electrostrictive coefficient (Q) increases with decreasing crystallinity.

I. INTRODUCTION

FROM the application point of view, electroactive polymers (EAPs) offer many advantages over ceramics and crystals, such as flexibility, low weight, low cost, and easy processing, to form complicated shapes. Electroactive polymers have attracted much attention for many years [1], [2], which resulted in the discovery of ferroelectric (FE) polymers as a new type of functional material. These polymers have been recognized to have potential applications in a variety of devices, such as transducers, actuators, and

sensors. However, in comparison with other existing functional materials, such as ceramics and single crystals [3], current FE polymers suffer low electroactivity, such as low electromechanical coupling coefficient and low strain energy density, which limit the applications of the materials.

To improve the material properties, there is interest in searching for new EAPs and modifying the existing materials. It was found that large strain response can be observed in some EAPs, such as heavily plasticized poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] and polyurethane [4]–[6]. However, the elastic modulus of these materials is low. In FE, it is well known that the defects have strong influence on the material properties. Recently, in an effort to study the effects of defects on, and to improve the material properties of, FE polymer, we showed that by making use of high energy electron irradiation, the P(VDF-TrFE) copolymers at a certain composition range exhibit a very large electrostrictive strain response ($\sim 5\%$) [7]–[9]. In addition to the large strain response, the irradiated P(VDF-TrFE) copolymers are of very high strain energy density ($\sim 0.5 \text{ J/cm}^3$ or $\sim 240 \text{ J/kg}$) because the elastic modulus is relatively high [7], [9]. In addition, in the DC electric field biased state, high piezoelectric coefficients ($d_{33} \sim -350 \text{ pm/V}$ and $d_{31} \sim 260 \text{ pm/V}$, which are comparable with those in ceramics) can be achieved [10]. More importantly from a material science point of view, the irradiated copolymer exhibits the features of typical relaxor FE [7], [11], [12]. Although inorganic relaxor FE have been widely studied in the last half century [13], no organic relaxor FE was reported before.

This paper presents the results of a detailed investigation on how the electromechanical properties (such as strain responses, polarization, and dielectric behavior) of the newly developed electrostrictive P(VDF-TrFE) copolymers with 50 mol% and 65 mol% VDF content [P(VDF-TrFE) 50/50 and 65/35] vary with different sample processing conditions prior to the irradiation, different electron treatment conditions, electric field driving conditions, and temperature. To elucidate what is responsible for these changes, data on microstructures and evolutions of the transitional phenomena will also be presented and analyzed. These results will be useful in guiding future work on improving the electroactive properties of the ma-

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materials and in designing the materials for different applications.

It is worthwhile to point out that in this study, P(VDF-TrFE) copolymers with VDF content at 70 mol% or higher were also investigated, and the results revealed that copolymers at those compositions cannot be converted to electrostrictive polymers with the 2.55-MeV electron source employed in this investigation. Therefore, only the results from the investigation on P(VDF-TrFE) 65/35 and 50/50 copolymers are presented.

II. EXPERIMENTS

P(VDF-TrFE) copolymer powders with a mean molecular weight of 200,000 were purchased from Solvay and Cie (Bruxelles, Belgium). Two approaches were used here to prepare the copolymer films, i.e., melt press and solution cast. In the melt press process, the P(VDF-TrFE) copolymer 50/50 and 65/35 powders were pressed between two pieces of aluminum foil at 215 and 225°C, respectively. The films were then either slowly cooled to room temperature, resulting in high crystallinity in the films, or quenched in ice cold water, to keep the crystallinity of the films low. In the solution cast method, the copolymer was dissolved in dimethylformamide (DMF) first and then the solution was cast on a flat glass plate and dried in an oven at 70°C. Two types of films were used in this investigation: the stretched and unstretched. In unstretched films, the prepared films were annealed at 140°C for a period between 12 to 14 h to improve the crystallinity. In stretched films, films made from solution cast or quenched from melt press were uniaxially stretched by a factor of 5 at a temperature between 25 and 50°C. Afterward, these films were also annealed at 140°C for 12 to 14 h to increase the crystallinity. To prevent shrinkage during the annealing for the stretched films, the two ends of the films were mechanically fixed during annealing. The thickness of both stretched and unstretched films was in the range of 15 to 30 μm . The irradiation was carried out in a nitrogen or argon atmosphere at different temperatures (from room temperature to 120°C) with 2.55-MeV electrons.

For the characterization of the dielectric properties, polarization, and electric field-induced strain behavior of the films, gold electrodes of thickness about 400 Å were sputtered on both surfaces of a film. The dielectric constant of the films under a weak electric field (~ 1 V) at frequencies from 30 to 100 kHz was measured by a dielectric analyzer (model no. 2970; TA Instruments, New Castle, DE) at temperatures from -60 to 120°C with a heating/cooling rate of 2°C/min. Because of the FE nature of the films, it is expected that the dielectric properties are strongly dependent on the driving field amplitude. In this investigation, the effective dielectric constant of films under high electric field was measured. In the measurement, the induced polarization in the film was computed from the current flowing through a resistor, which is in series with the film and whose electric impedance is much smaller (more

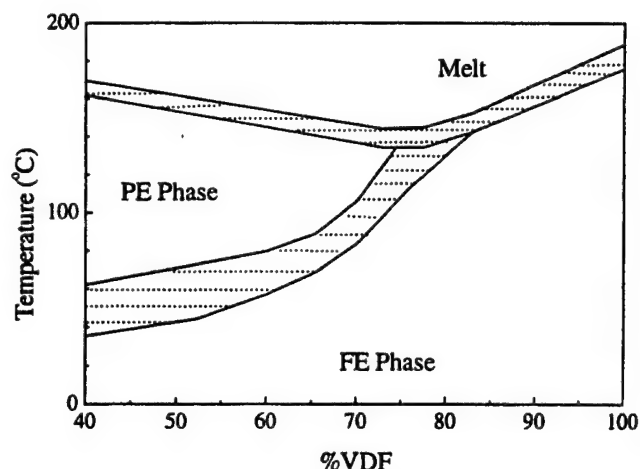


Fig. 1. Phase diagram of P(VDF-TrFE) copolymer. The exact phase transition temperature depends on sample fabrication, sample thermal treatment, and processing history. The dashed areas correspond to the phase transition temperature region.

than 10,000 times smaller) than that of the film. The polarization hysteresis loop was measured by a computer-controlled automatic system based on the Sawyer-Tower circuit. The longitudinal strain, the strain response along the thickness direction, was characterized by a strain sensor, which was designed specifically for the polymer film strain measurements, based on the piezoelectric bimorph sensor [14]. The transverse strain, the strain response along the film surface, was measured using a cantilever-based dilatometer that was newly developed for characterizing transverse strain response of polymer film under external electric fields [12].

Differential scanning calorimeter (DSC) measurements were performed to monitor the change of crystallinity with different irradiation conditions and were carried out at a scanning rate of 10°C/min under a nitrogen atmosphere using a DSC (model no. 2010; TA Instruments) from -60 to 200°C. The elastic modulus of the films was characterized along the film direction (perpendicular to the film thickness) using a dynamic mechanical analyzer (DMA) (model no. 2980; TA Instruments) in the temperature range from -60 to 100°C at different frequencies.

III. RESULTS AND DISCUSSION

A. Polarization, Dielectric Properties, and DSC Data

At room temperature, P(VDF-TrFE) copolymer is a normal ferroelectric whose phase diagram is shown in Fig. 1. There is a melting transition at temperatures above 150°C and a clear FE to paraelectric (PE) phase transition for most of the copolymer compositions (at compositions below 85 mol% VDF) [1], [15]. A typical polarization hysteresis loop taken from P(VDF-TrFE) 65/35 copolymer is shown in Fig. 2(a). In most of the electromechanical applications, the material is operated near the

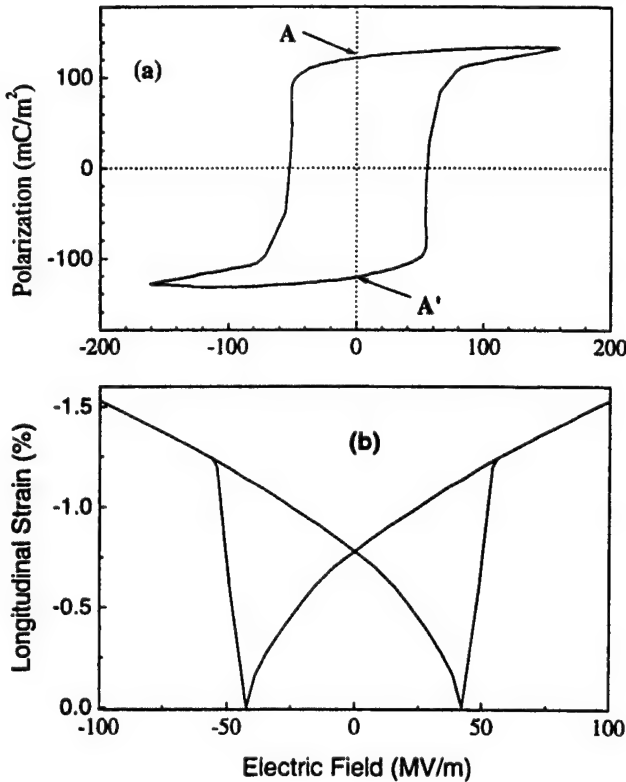


Fig. 2. Typical polarization and strain responses in P(VDF-TrFE) 65/35 copolymer at ferroelectric phase: a) polarization vs. electric field and b) longitudinal strain vs. electric field.

point A or A', and the strain response (S) is linearly proportional to the applied electric field (E in V/m) (piezoelectric response) [2]:

$$S_{ij} = d_{ijk} E_k \quad (1)$$

where d_{ijk} (in m/V) is the piezoelectric strain coefficient. By switching the polarization through the polarization hysteresis, a larger strain response can be obtained as shown in Fig. 2(b), where a strain of about -1.5%, which is much higher than the strain level in the piezoelectric state, can be achieved for the P(VDF-TrFE) 65/35 copolymer. However, the strain response of Fig. 2(b) type is not desirable and may not be used in practical devices because it involves a high hysteresis and also because the large polarization hysteresis will cause severe dielectric loss, resulting in sample heating.

The large hysteresis observed in a normal ferroelectric P(VDF-TrFE) copolymer is due to the high nucleation barrier when switching polarization from coherent macroscopic polar domains [1], [2]. By breaking this macroscopic coherent polar domain, one can reduce or eliminate the polarization hysteresis. This is the reason behind the observed evolution from the large hysteresis polarization loop to a slim polarization loop when a P(VDF-TrFE) copolymer is irradiated with proper doses of high energy electrons [7], [10], [11]. That is, the electron irradiation breaks up the coherent polarization domains in the crystalline re-

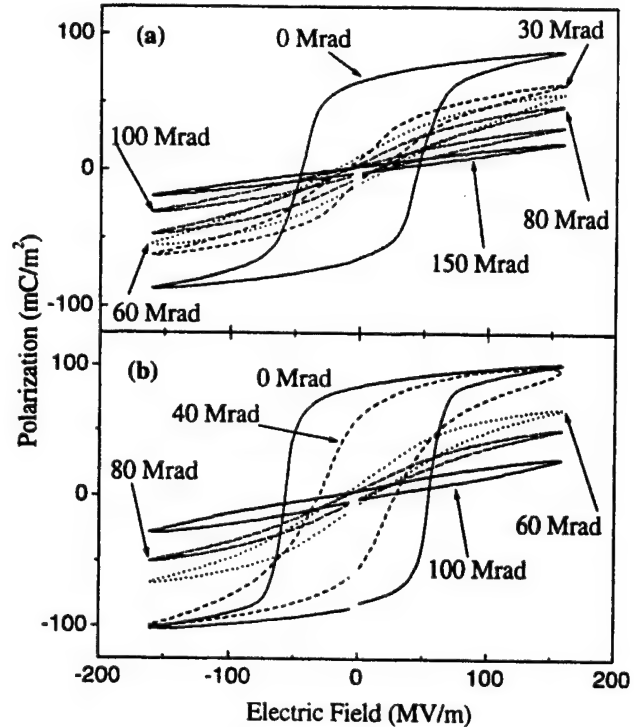


Fig. 3. Polarization hysteresis loops at 10 Hz of P(VDF-TrFE) copolymer films measured at room temperature for a) unstretched 50/50 films irradiated at 120°C and b) unstretched 65/35 films irradiated at 120°C with different irradiation dosages.

gion into nanopolar regions. The data shown in Fig. 3 is the change of the polarization hysteresis loop with electron dosage for the unstretched copolymer films irradiated at 120°C, where Fig. 3(a) is for 50/50 films and Fig. 3(b) is for 65/35 films. With increasing dosage, the polarization loop becomes slim with little hysteresis. For the copolymers with a slim hysteresis loop, the dielectric constant measured at a weak electric field (~ 0.04 MV/m) exhibits a broad peak at a temperature near room temperature as shown in Fig. 4. In addition, the peak position shifts with frequency, and the relationship between the peak temperature (T_m) and frequency can be described by the Vogel-Fulcher law quite well [7], [11]. Therefore, these experiment results suggest that the irradiated copolymer obtained here belongs to a special class of ferroelectrics, i.e., relaxor ferroelectrics [13], [16]. That is, the high energy irradiation transforms the crystalline phase from a normal FE into a relaxor FE.

Fig. 3 also reveals that as the dosage increases, the induced polarization level under a given applied field reduces, and, at a high dosage, the polarization level becomes much smaller than that in an unirradiated sample. This is a result of the reduction of the crystallinity in the polymer with irradiation. Presented in Fig. 5 is the DSC data for both 65/35 and 50/50 copolymers under different doses. For unirradiated films, there are two well-defined peaks. The one at temperatures above 150°C is associated with the melting of the crystallites, and the low temperature one

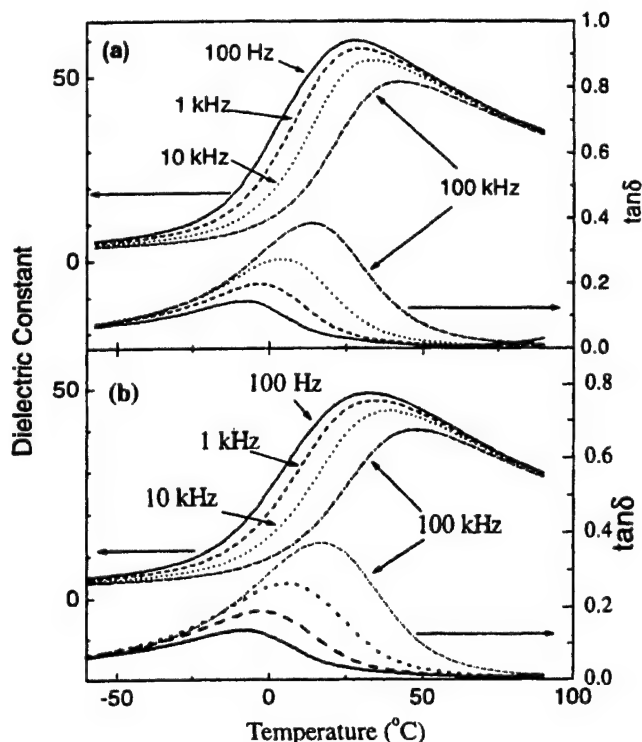


Fig. 4. Temperature dependence of the dielectric constant and loss at different frequencies (100 Hz, 1 k, 10 k, and 100 kHz) for irradiated P(VDF-TrFE) copolymer films: a) stretched 65/35 mol% irradiated at 95°C with 60 Mrad dosage, b) stretched 50/50 mol% irradiated at 95°C with 40 Mrad dosage.

is from the FE-PE transition. The enthalpy of the melting can be used as a measure of the crystallinity of the film. It is found that the crystallinity of both stretched and unstretched copolymer films before irradiation is about 75%. The data in Fig. 5 show that with increased dosage, the area under the melting peak (enthalpy of the melting) decreases, and, for the 50/50 copolymer at the 150-Mrad dosage, this peak disappears, indicating that the polymer is more or less amorphous. Therefore, in addition to transforming the crystalline region of the polymer from a normal FE with large polarization hysteresis to a relaxor FE with slim polarization loop, high energy electron irradiation also converts the crystalline phase into amorphous phase, and, as a result, the field induced polarization level is reduced. These are two competing processes, and how to increase one process (transformation in the crystalline region) and reduce the reduction of the crystallinity with dose is still a challenge. Because the electric field-induced strain in the material is proportional to the polarization level, a high crystallinity is clearly highly desirable to achieve a high strain and high elastic energy density. A way to increase the electric field-induced strain response of the irradiated material is varying irradiation condition, such as the electron energy, irradiation temperature, and dosage. The effect of the irradiation temperature, and dosage on the strain response of the copolymer will be

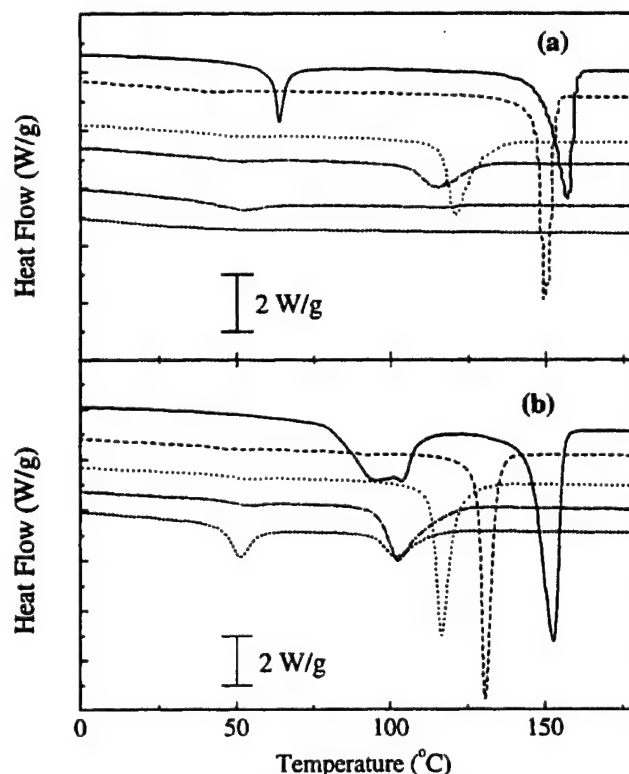


Fig. 5. Enthalpy change of the melting point of crystallites in a) unstretched P(VDF-TrFE) 50/50 irradiated at 120°C (from top to bottom curve, dosage is 0, 30, 60, 80, 100, and 150 Mrad, respectively) with the irradiation dosage and b) unstretched P(VDF-TrFE) 65/35 irradiated at 95°C (from top to bottom curve, dosage is 0, 60, 80, 100, and 120 Mrad, respectively).

presented in the following section. With regard to the irradiation energy, we recently found that using the electron beam with a low energy of (1.0~1.2 MeV) for irradiation seems better than using that 2.55 MeV. Further detailed studies of the electron energy effect will be carried out. To transform the crystalline region from normal FE to relaxor FE, besides irradiation, other possible approaches are introducing chemical defects in the polymer chain or using different thermal treatment processes, such as quenching, to treat the material to introduce defects.

B. Field-Induced Strain Responses in Irradiated Copolymers

Presented in Fig. 6 is the relationship between the electric field-induced longitudinal strain and electric field from P(VDF-TrFE) 65/35 copolymer irradiated at 120°C with a 80-Mrad dosage. The film was made from a solution cast with DMF and stretched. The data shows that, in irradiated films, an ultrahigh field-induced strain can be induced. From a recent x-ray diffraction experiment, it was observed that the field-induced strain in the relaxor FE P(VDF-TrFE) copolymer is mainly due to the field-induced local phase, transformation between the non-polar

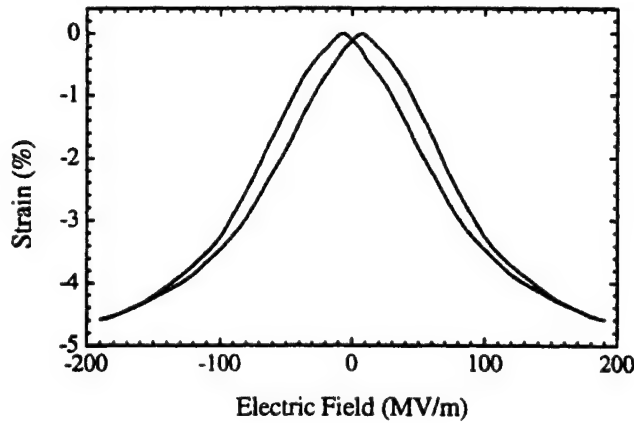


Fig. 6. Longitudinal strain vs. electric field in P(VDF-TrFE) 65/35 copolymer irradiated at 120°C with 80 Mrad dosage.

phase and polar phase, which involves a very high lattice strain [17]. This is different from the strain observed in polarization switching in a normal FE P(VDF-TrFE) copolymer [Fig. 2(b)], where the strain is mainly due to the polarization reorientation between different domain states.

In an FE polymer, the electric field-induced strain response is closely related to the polarization in the material. Being a semicrystalline polymer, this response is affected by the crystallinity. Because the high energy electron irradiation influences both the crystallite polarization and crystallinity, as shown in the proceeding section, it is expected that the electric field-induced strain will be sensitive to the electron irradiation conditions such as dosage, irradiation temperature, and electron energy. Presented in Fig. 7 is the amplitude of the longitudinal strain S_3 vs. the amplitude of the applied field measured at 1 Hz at room temperature for the irradiated 65/35 copolymers, which exhibit slim polarization loops. In the figures, the results from both stretched and unstretched films are shown. Similar results for the irradiated 50/50 copolymers are presented in Fig. 8.

Because the copolymer film studied here is a semicrystalline polymer, effective electrostrictive coefficients Q_{ij} (effective charge-related electrostrictive coefficients) are introduced to describe phenomenally this polarization dependence behavior [18]:

$$S_3 = Q_{33}P^2 \quad (2a)$$

$$S_1 = Q_{13}P^2 \quad (2b)$$

where P is the polarization, S_3 is the longitudinal strain, and S_1 is the transverse strain. For stretched film, S_1 is the transverse strain along the stretch direction. For the irradiated copolymer exhibiting a slim polarization loop, it has been shown that in the entire polarization range, the electric field-induced strain (S) is proportional to the square of polarization (P) [8]. That is, as will be presented subsequently, the value of Q is independent of the electric

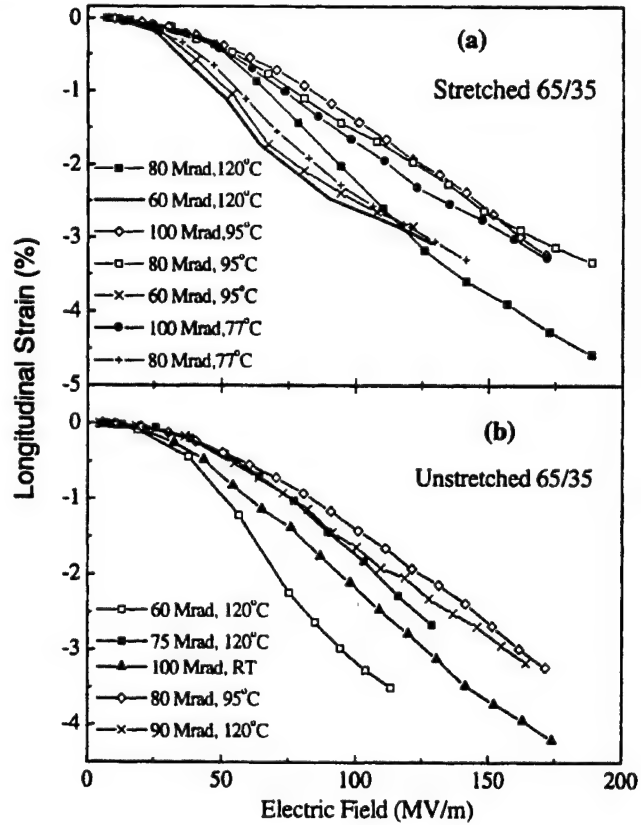


Fig. 7. Longitudinal strain amplitude vs. electric field amplitude in P(VDF-TrFE) 65/35 mol% copolymer films obtained at 1 Hz at room temperature: a) stretched films and b) unstretched ones.

field. For a linear dielectric material, (2) can be converted to the applied electric field (E),

$$S_3 = M_{33}E^2 \quad (3a)$$

$$S_1 = M_{13}E^2 \quad (3b)$$

where M_{ij} is the effective electric field-related electrostrictive coefficient and M_{ij} and Q_{ij} are related by the dielectric constant. In the following discussion, Q_{ij} and M_{ij} are termed as charge and field electrostrictive coefficients, respectively, for simplicity. For the copolymers investigated here, as shown in Fig. 3, the polarization is not a linear function of field, and (3) may not describe the $S \sim E$ relationship precisely. For comparison of different materials, we will still use M_{ij} to measure the effectiveness of the material in generating strain under a given field. M_{ij} presented in the following is defined as

$$S_{ap} = M_{ij}E_{ap}^2 \quad (4)$$

where S_{ap} and E_{ap} are the amplitude of the strain and the corresponding applied electric field amplitude, respectively. In Table I, M_{33} calculated for the longitudinal strain of the copolymers examined are presented for both 65/35

TABLE I
ELECTROSTRICTIVE COEFFICIENT ($-M_{33} \times 10^{18} \text{ m}^2/\text{V}^2$) AT DIFFERENT
ELECTRIC FIELDS AND Q_{33} FOR DIFFERENT SAMPLES.

Stretched 65/35	$-M_{33}$			$-Q_{33}$ (m^4/C^2)
	50 MV/m	100 MV/m	150 MV/m	
60 Mrad, 120°C	4.20	2.25	1.6*	5.4 (± 0.3)
80 Mrad, 120°C	1.75	2.23	1.68	9.0 (± 0.3)
100 Mrad, 95°C	1.50	1.39	1.16	6.0 (± 0.4)
80 Mrad, 95°C	1.63	1.54	1.1	7.2 (± 0.2)
60 Mrad, 95°C	3.58	2.53	1.4*	4.5 (± 0.4)
120 Mrad, 77°C	1.92	1.46	1.10	10.0 (± 0.3)
100 Mrad, 77°C	1.76	1.69	1.25	8.6 (± 0.3)
80 Mrad, 77°C	3.00	2.43	1.57	4.6 (± 0.2)
160 Mrad, RT	0.47	1.04	0.80	
120 Mrad, RT	0.37	1.17	0.94	
Unstretched				
65/35				
60 Mrad, 120°C	3.57	3.17	1.7*	12.0 (± 0.5)
75 Mrad, 120°C	1.52	1.74	1.5*	
90 Mrad, 120°C	1.65	1.63	1.24	7.14 (± 0.3)
80 Mrad, 95°C	1.49	1.39	1.17	7.5 (± 0.3)
100 Mrad, RT	2.70	2.19	1.63	9.0 (± 0.3)
140 Mrad, RT	1.54	1.31	1.06	5.7 (± 0.2)
180 Mrad, RT	0.64	1.12		
Unstretched				
50/50				
80 Mrad, RT	1.85			
100 Mrad, RT	2.01	1.97	1.58	8.0 (± 0.7)
120 Mrad, RT	0.56	0.57	0.53	5.7 (± 0.2)
35 Mrad, 120°C	4.50	2.00		
40 Mrad, 120°C	5.10	2.10	1.20	9.9 (± 0.2)
70 Mrad, 120°C	1.30	1.17	0.97	10.6 (± 0.3)
Stretched				
50/50				
40 Mrad, 95°C	1.15	0.91	0.73*	4.2 (± 0.2)
60 Mrad, 77°C	2.23	2.11	1.56	11.8 (± 0.3)
35 Mrad, 120°C	4.04	2.20	1.50	13.0 (± 0.5)
40 Mrad, 120°C	3.74	1.65*		
80 Mrad, RT	1.45	1.31	1.0*	12.8 (± 0.5)
70 Mrad, RT	1.55	1.28		

*The data were extrapolated to the electric field.

and 50/50 compositions under different irradiation conditions for three driving field amplitudes, 50, 100, and 150 MV/m. Because of the nonlinear relationship between P and E , M_{33} varies with the field amplitude. The data in Table I reveal that, in most cases, for the slim loop copolymers, M_{33} decreases with dosage, which is consistent with the result in Fig. 3, where the induced polarization decreases with dosage. Because of the nonlinear relationship between P and E and the saturation of P at high fields, there are deviations from this general rule. To illustrate these features more clearly, M_{33} as a function of dosage under different applied field amplitude is presented in Fig. 9 for selected copolymers.

The copolymers in Table I can be divided into four groups: stretched films of 65/35, stretched films of 50/50,

unstretched films of 65/35, and unstretched films of 50/50. Among the irradiation conditions investigated for each group, there is one irradiation condition that yields the highest M_{33} and, hence, the highest longitudinal strain. Based on the DSC data, it is found that the crystallinity of the samples exhibiting high strain response is about 60%. In Fig. 10, M_{33} from the best performed samples of each group is plotted as a function of applied field amplitude. The data in the figure indicate the following interesting features. 1) At low fields, stretched films yield better strain response than unstretched films; at high fields, this difference is not significant. 2) 65/35 copolymer generates higher strain response than 50/50 copolymer. Therefore, considering the reduced manufacturing cost and increased reliability of unstretched films, 65/35 unstretched films should

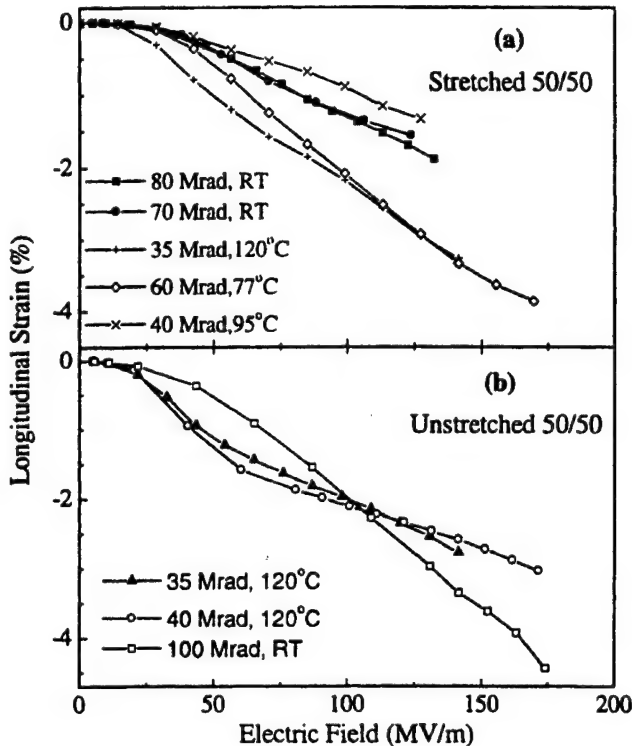


Fig. 8. Longitudinal strain amplitude vs. electric field amplitude in P(VDF-TrFE) 50/50 mol% copolymer films obtained at 1 Hz at room temperature: a) stretched ones and b) unstretched ones.

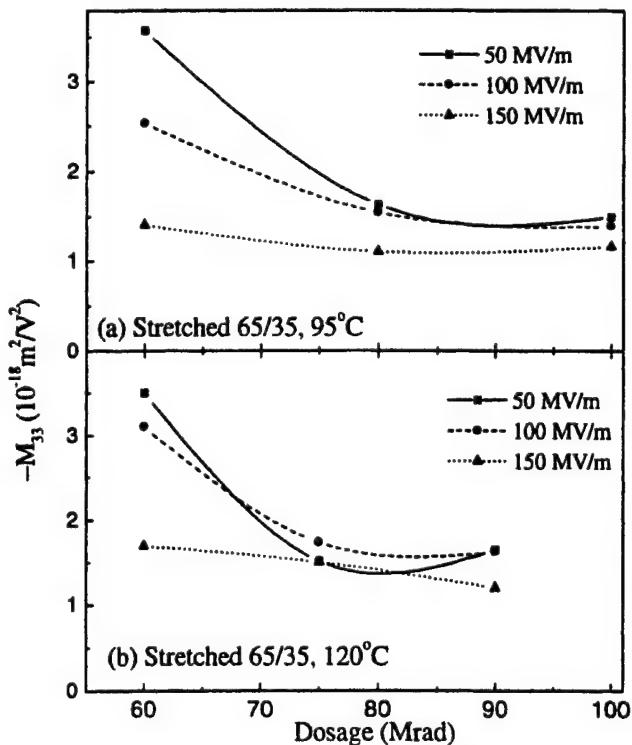


Fig. 9. Value of M_{33} vs. dosage for the different samples: a) stretched 65/35 irradiated at 95°C and b) unstretched 65/35 irradiated at 120°C.

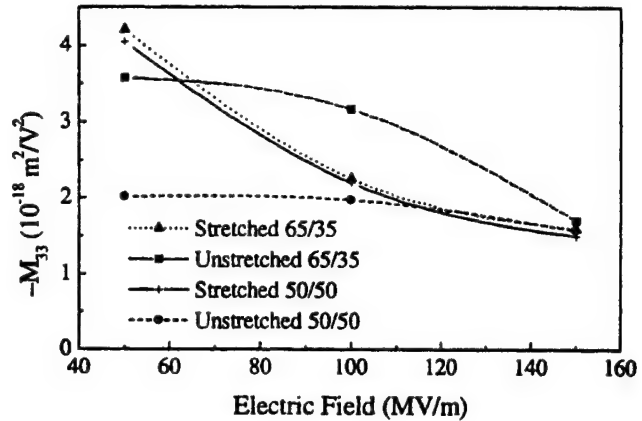


Fig. 10. Values of M_{33} vs. electric field for the sample with the best performance in each group from Table I.

be preferred for the longitudinal strain electromechanical transducer applications. As will be discussed, one additional reason for choosing unstretched films for longitudinal electromechanical transducer application is the very low transverse strain response in unstretched films.

Now we discuss the results from the transverse strain responses of the irradiated copolymers with slim polarization loop. For unstretched films, the transverse strain is quite small, and, in most of the films examined, the amplitude ratio between the transverse strain (S_1) and longitudinal strain is less than 0.33. This feature is attractive for many devices utilizing the longitudinal strain, such as ultrasonic transducers in the thickness mode and actuators and sensors making use of the longitudinal electromechanical responses of the material. For example, a very weak transverse electromechanical response in comparison with the longitudinal one can significantly reduce the influence of lateral modes on the thickness resonance and improve the performance of the transducer.

On the other hand, for stretched films, a large transverse strain can be achieved as shown in Fig. 11, which is taken from the strain measured along the stretch direction for 65/35 and 50/50 copolymers. The M_{13} coefficient from the transverse strain (S_1) along the stretch direction for both 65/35 and 50/50 copolymer films under different irradiation conditions is summarized in Table II. Comparison between Table I and Table II indicates that $|S_1|$ can reach as high as $|S_3|$ (e.g., 65/35 irradiated at 95°C). In addition, S_1 from the 65/35 copolymer is much higher than that from 50/50 copolymer, as shown in Fig. 12, which is different from the longitudinal strain where the difference is not so large. Hence, for transverse strain actuation applications, stretched 65/35 copolymer is the clear choice.

C. Effective Charge Related Electrostrictive Coefficients

Although M_{ij} varies with the applied field amplitude as discussed previously, it is found that the charge electrostrictive coefficient (Q) remains constant in the same electric field range. The experimental results for the

TABLE II
ELECTROSTRICTIVE COEFFICIENT ($M_{13} \times 10^{18} \text{m}^2/\text{V}^2$) AT DIFFERENT
ELECTRIC FIELDS AND Q_{13} FOR DIFFERENT SAMPLES.

Stretched 50/50	M_{13}			Q_{13} (m^4/C^2)
	50 MV/m	100 MV/m	150 MV/m	
60 Mrad, 77°C	1.22	0.95	0.6*	4.3 (± 0.2)
40 Mrad, 95°C	1.59	0.91	0.46*	2.6 (± 0.2)
60 Mrad, 95°C	1.14	1.03	0.80*	6.4 (± 0.3)
80 Mrad, 95°C	0.635	0.627		
100 Mrad, 95°C	0.53	0.57	0.50	11.0 (± 0.4)
Stretched 65/35				
80 Mrad, 77°C	2.30	1.95		
100 Mrad, 77°C	1.01			
120 Mrad, 77°C	1.18	1.21	1.14*	10.3 (± 0.4)
60 Mrad, 95°C	3.27	2.75*		4.6 (± 0.2)
80 Mrad, 95°C	1.41	1.53*		6.9 (± 0.3)
100 Mrad, 95°C	1.32	1.37	1.02	6.5 (± 0.3)

*The data were extrapolated to the electric field.

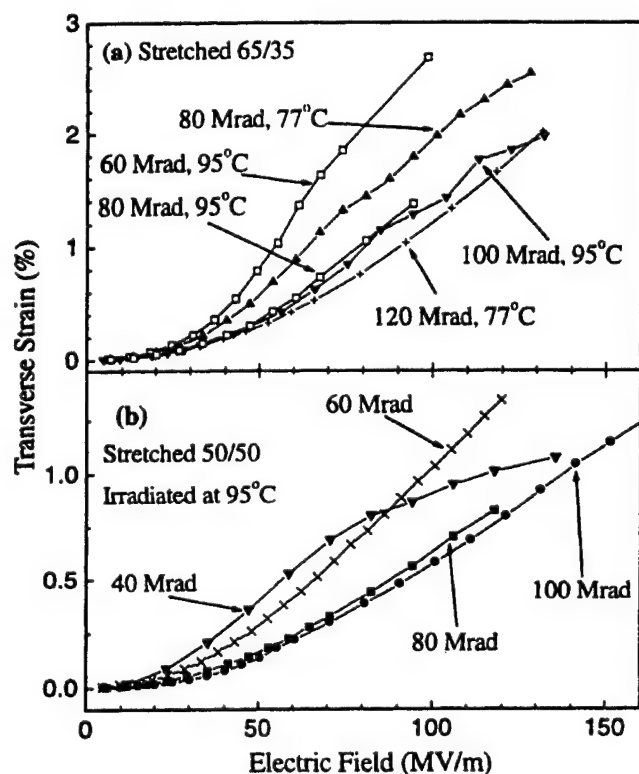


Fig. 11. Transverse strain amplitude vs. electric field amplitude in stretched P(VDF-TrFE) copolymer films obtained at 1 Hz at room temperature: a) 65/35 and b) 50/50. The transverse strain is the strain response along the stretching direction.

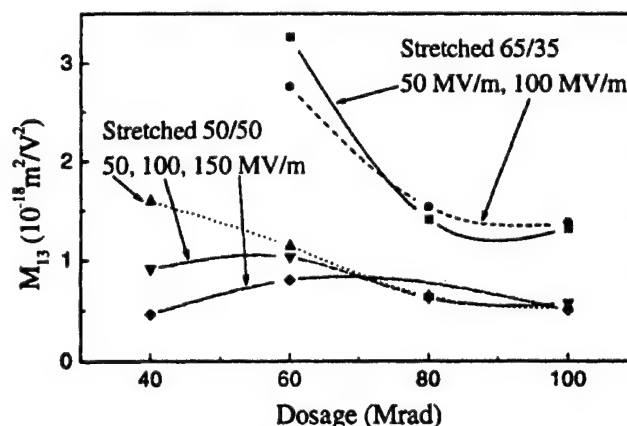


Fig. 12. Value of M_{13} vs. dosage for samples with the best performance in the stretched 50/50 and 65/35, respectively.

stretched 65/35 copolymer film irradiated at 95°C with 60 Mrad are shown in Fig. 13(a) and (b) for the electric field dependence of M_{13} and Q_{13} , respectively. The constant of Q indicates that the relationship between strain response and the polarization square is indeed linear as described by (2). This indicates that the change in M_{ij} with field is indeed caused by the nonlinear $P \sim E$ relationship. To illustrate this, in Fig. 13(c), the change of the effective dielectric constant with driving field amplitude for the same copolymer is presented.

The values of Q_{ij} determined using (2) are also listed in Table I and Table II. It appears that there is no significant difference in Q_{ij} between 50/50 copolymer and 65/35 copolymer. However, there seems to be a trend that the amplitude of Q_{ij} in films with higher induced polarization (hence, higher crystallinity) is smaller than that in films with lower induced polarization. This is shown in Fig. 14, where the polarization level (P_m) for the samples under an

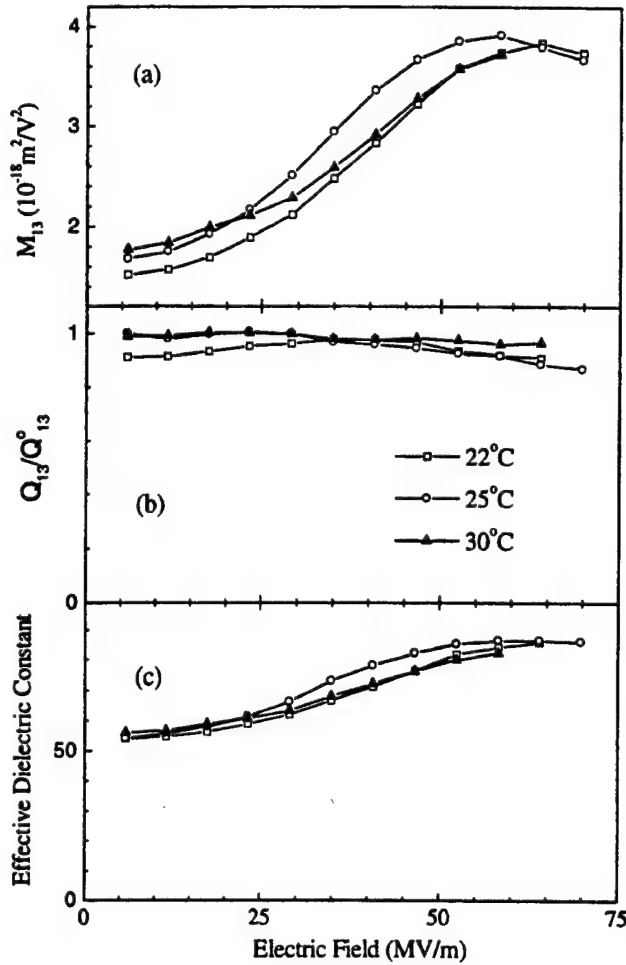


Fig. 13. Electric field dependence of some physical constants at room temperature in stretched 65/35 copolymer film irradiated at 95°C with 60 Mrad: a) M_{13} vs. electric field, b) Q_{13} vs. electric field, and c) effective dielectric constant vs. electric field.

external electric field of 150 MV/m is used. In other words, under the same irradiation temperature, $|Q_{ij}|$ increases with dosage (except for those irradiated at room temperature). Furthermore, the $|Q_{ij}|$ obtained here seems higher than those predicted for the intrinsic single crystal values of P(VDF-TrFE) copolymers [19]. The behaviors observed here can be qualitatively understood by the morphology of the copolymer, which is a semicrystalline polymer.

To illustrate this, consider the hydrostatic electrostrictive coefficient (Q_h) as an example where $S_v = Q_h P^2$ and S_v is the volume strain. For a polymer with a composite morphology, the total volume strain S_v will be the summation of that from the crystalline phase S_{Cv} and the amorphous phase S_{Av} :

$$S_v = v_C S_{Cv} + v_A S_{Av} \quad (5)$$

where v_C and $v_A (= 1 - v_C)$ are the volume fraction of the crystalline and amorphous phases. From an early study, it was found that in the irradiated P(VDF-TrFE) copolymer, the total polarization P measured from a film can

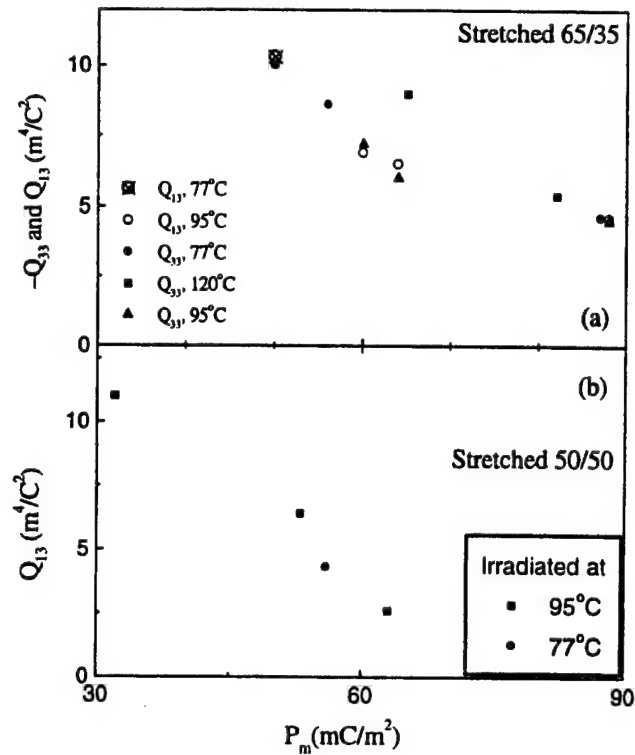


Fig. 14. Q_{33} and Q_{13} vs. polarization level of the samples under an external electric field of 150 MV/m: a) stretched 65/35 films and b) stretched 50/50 films.

be related to the polarization in the crystalline phase P_C and amorphous phase P_A by the logarithmic law of mixing observed for many diphas 0-3 composites [20]:

$$\text{Log}(P) = v_C \text{log}(P_C) + v_A \text{log}(P_A) \quad (6)$$

In the crystalline region and amorphous, we will have

$$S_{Cv} = Q_{hC} P_C^2 \quad (7a)$$

$$S_{Av} = Q_{hA} P_A^2 \quad (7b)$$

where Q_{hC} and Q_{hA} are the effective hydrostatic electrostrictive coefficients in the crystalline and amorphous regions, respectively. Combining (5) to (7) yields

$$Q_h = Q_{hC} \left\{ v_C n^{2(1-v_C)} + \frac{Q_{hA}}{Q_{hC}} \frac{1-v_C}{n^{2v_C}} \right\} \quad (8)$$

where $n = P_C/P_A$. From the pyroelectric study of the uniaxially stretched PVDF, it was found that the value of n is about 7.5 [21]. For the irradiated P(VDF-TrFE) 50/50 copolymer, it was found that the value of n is about 9.0 [20]. Using $n = 8$ as an example here, the ratio of Q_h/Q_{hC} as a function of the crystallinity v_C in the polymer is presented in Fig. 15 using (8), where the ratios of Q_{hA}/Q_{hC} with 0.5, 1, and 2 were used. The figure shows that over most of the crystallinity range, the ratio of Q_h/Q_{hC} is larger than 1, and it seems that this result is not very sensitive to the Q_{hA} value of the amorphous phase. That is,

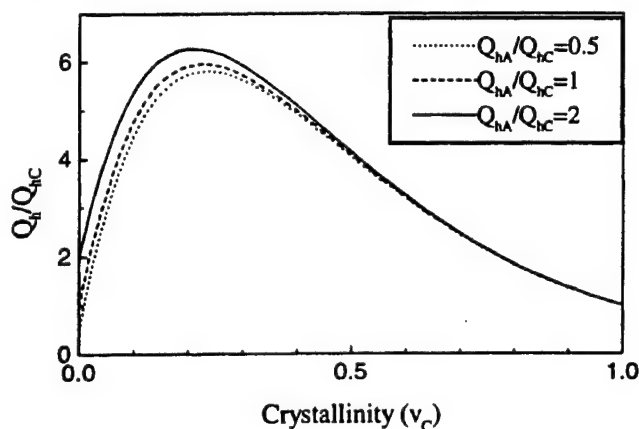


Fig. 15. Crystallinity (v_c) dependence of calculated Q_h through (7) where $n = 8$ is used and Q_{hA}/Q_{hC} is 0.5, 1, and 2, respectively.

the measured electrostrictive coefficient from the composite is higher than that of the crystallite when $P_C/P_A \gg 1$, which may be consistent with the observation here that the measured electrostrictive coefficients increase with irradiation doses.

In (7b), Q_{hA} is used as an effective electrostrictive coefficient to describe the $S \sim P$ relationship in the amorphous region. In reality, the Maxwell stress-induced strain response, which is due to the Coulombic force between the free charges in the electrodes, can be quite significant in an amorphous polymer [6], [22], [23]. Therefore, the effective coefficient Q_{hA} also includes the contribution from this part, and, in the measured total electrostrictive coefficient Q , there will be contributions from the Maxwell stress. In the samples with very high irradiation dosages, which result in a low crystallinity, the contribution from the Maxwell stress effect can be significant. However, as has been discussed in an early publication and also revealed by a recent X-ray study of irradiated films under different electric fields [7], [12], [17], in the irradiated copolymers with very high strain responses, the main contribution is due to the local FE transformation and hence, the field-induced strain is electrostrictive in nature.

The temperature dependence of the electric field-induced strain in the irradiated copolymers was also studied. Presented in Fig. 16(a) is the transverse strain along the stretching direction for 65/35 copolymer irradiated at 95°C with 60 Mrad. The electric field induced strain increases with reduced temperature and reaches a broad peak at just below room temperature. For comparison, the elastic modulus along the stretching direction is also shown in Fig. 16(b). The increase of the field-induced strain with reduced temperature and the existence of a broad peak are typical signatures of relaxor FE associated with the increase of the local polarization in the material and increased normal FE behavior as the temperature is lowered [24]. This is clear experimental evidence that in the copolymers studied here, the strain response is from the local polarization and hence, electrostrictive. If the strain

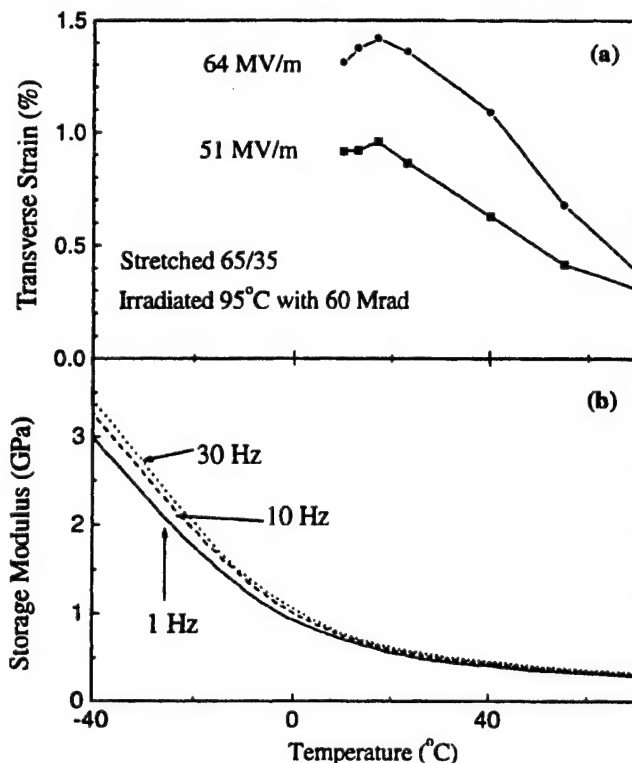


Fig. 16. For the stretched 65/35 film irradiated at 95°C with 60 Mrad: a) temperature dependence of the transverse strain along the stretch direction at different electric fields and b) temperature dependence of the elastic modulus along the stretching direction at different frequencies.

response is mainly from the Maxwell stress effect, as has been observed in the field-induced strain response in a polyurethane elastomer [23], [25], one would expect a decrease of the field-induced strain as the temperature is reduced because the elastic modulus increases as the temperature is lowered.

IV. SUMMARY

The effect of high energy electron (2.55 MeV) irradiation on the polarization and dielectric behaviors and the electromechanical properties of P(VDF-TrFE) 50/50 and 65/35 copolymer films is reported. The results show that the electron irradiation transforms the normal FE P(VDF-TrFE) copolymer into a relaxor FE with ultra-high electrostrictive strain. It also shows that in addition to this transformation, the irradiation also converts the crystalline phase into amorphous phase, causing a reduction in the polarization level of the polymer. To further increase the strain response and elastic energy density, it is necessary to reduce this latter process.

Among the two copolymers investigated, we found that the 65/35 copolymer is preferred for both longitudinal and transverse strain generation. Although the difference in the longitudinal strains generated by 65/35 and 50/50 copoly-

mers is not very large, the transverse strain along the stretching direction from 65/35 is much larger than that from 50/50 copolymer. Among the copolymers exhibiting slim polarization hysteresis loop and electrostrictive strain, we found that, in general, the electric field-induced strain decreases as the irradiation dosage increases, caused by the reduction of the crystallinity in the polymer by the irradiation. This, plus the temperature dependence of the field-induced strain, indicates that the electric field-induced strain is due to the responses of local polar regions in the relaxor P(VDF-TrFE) copolymer and, hence, confirms the electrostrictive nature of the strain response. As a result of this and the semicrystalline morphology of the copolymers, the effective charge-related electrostrictive coefficient (Q) measured from irradiated copolymers is higher than those from the intrinsic crystalline phase and shows an increase with the irradiation dosages. A simple model is presented to support this observation.

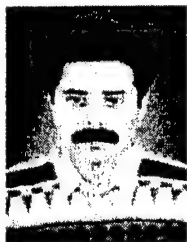
REFERENCES

- [1] H. S. Nalwa, *Ferroelectric Polymers*. New York: Dekker, 1995.
- [2] T. T. Wang, J. M. Herbert, and A. M. Glass, *Applications of Ferroelectric Polymers*. New York: Chapman and Hall, 1988.
- [3] L. E. Cross, "Ferroelectric ceramics: Materials and application issues," *Ceramic Trans.*, vol. 68, pp. 15-55, 1996.
- [4] Z. Ma, J. I. Scheinbein, and B. A. Newman, "Electrostrictive response of elastomeric polymers," *Polymer Reprints*, vol. 33, pp. 385-386, 1992.
- [5] Z. Ma, J. I. Scheinbein, and B. A. Newman, "High field electrostrictive response of polymers," *J. Polym. Sci. Part B, Polym. Phys.*, vol. 32, pp. 2721-2731, 1994.
- [6] R. E. Pelrine, R. D. Kornbluh, and J. P. Joseph, "Electrostriction of polymer dielectrics with compliant electrodes as a mean of actuation," *Sens. Actuators A*, vol. 64, pp. 77-85, 1998.
- [7] Q. M. Zhang, V. Bharti, and X. Zhao, "Giant electrostriction and relaxor ferroelectric behavior in electron-irradiated poly(vinylidene fluoride-trifluoroethylene) copolymer," *Science*, vol. 280, pp. 2101-2104, 1998.
- [8] X. Zhao, V. Bharti, Q. M. Zhang, T. Romotowski, F. Tito, and R. Ting, "Electromechanical properties of electrostrictive poly(vinylidene fluoride-trifluoroethylene) copolymer," *Appl. Phys. Lett.*, vol. 73, pp. 2054-2056, 1998.
- [9] Z.-Y. Cheng, T.-B. Xu, V. Bharti, S. Wang, and Q. M. Zhang, "Transverse strain responses in the electrostrictive poly(vinylidene fluoride-trifluoroethylene) copolymer," *Appl. Phys. Lett.*, vol. 74, pp. 1901-1903, 1999.
- [10] Z.-Y. Cheng, V. Bharti, X. Zhao, S. Wang, T.-B. Xu, and Q. M. Zhang, "Relaxor ferroelectric polymers for actuators and transducers," *Proc. IEEE Ultrason. Symp.*, Miyagi, Japan, 1998, pp. 581-584.
- [11] V. Bharti, X. Zhao, Q. M. Zhang, T. Ramotowski, F. Tito, and R. Ting, "Ultrahigh field induced strain and polarization response in electron irradiated poly(vinylidene fluoride-trifluoroethylene) copolymer," *Mater. Res. Innovat.*, vol. 2, pp. 57-63, 1998.
- [12] Z.-Y. Cheng, V. Bharti, T.-B. Xu, S. Wang, Q. M. Zhang, T. Ramotowski, F. Tito, and R. Ting, "Transverse strain response in electrostrictive poly(vinylidene fluoride-trifluoroethylene) films and development of a dilatometer for the measurement," *J. Appl. Phys.*, vol. 86, pp. 2208-2214, 1999.
- [13] L. E. Cross, "Relaxor ferroelectrics: an overview," *Ferroelectrics*, vol. 151, pp. 305-320, 1994.
- [14] J. Su, P. Mouse, and Q. M. Zhang, "A bimorph based dilatometer for field induced strain measurement in soft and thin free standing polymer films," *Rev. Sci. Instrum.*, vol. 69, pp. 2480-2483, 1998.
- [15] F. J. Balta, A. G. Arche, T. A. Ezquerro, C. S. Cruz, F. Bataillon, B. Frick, and E. L. Cabarcos, "Structure and properties of ferroelectric copolymer poly(vinylidene fluoride)," *Prog. Polym. Sci.*, vol. 18, pp. 1-48, 1993.
- [16] Z.-Y. Cheng, R. S. Katiyar, X. Yao, and A. Guo, "Dielectric behavior of lead magnesium niobate relaxors," *Phys. Rev. B*, vol. 55, pp. 8165-8174, 1997.
- [17] Q. M. Zhang, Z.-Y. Cheng, and V. Bharti, "Relaxor ferroelectric behavior in high energy electron irradiated poly(vinylidene fluoride-trifluoroethylene) copolymers," *Appl. Phys. A*, vol. 70, pp. 307-312, 2000.
- [18] F. Jona and G. Shirane, *Ferroelectric Crystals*. New York: Dover Publications, 1993.
- [19] T. Furukawa, "Ferroelectric properties of vinylidene fluoride copolymers," *Phase. Trans.*, vol. 18, pp. 143-211, 1989.
- [20] V. Bharti, H. S. Xu, G. Shanthi, Q. M. Zhang, and K. Liang, "Polarization and structural properties of high energy electron irradiated poly(vinylidene fluoride-trifluoroethylene) copolymer films," *J. Appl. Phys.*, vol. 87, pp. 452-461, 2000.
- [21] D. Rollik, S. Bauer, and R. Gerhard-Multhaut, "Separate contributions to the pyroelectricity in poly(vinylidene fluoride) from the amorphous and crystalline phases, as well as from their interface," *J. Appl. Phys.*, vol. 85, pp. 3282-3288, 1999.
- [22] Y. M. Shkel and D. J. Klingenberg, "Material parameters for electrostriction," *J. Appl. Phys.*, vol. 80, pp. 4566-4572, 1996.
- [23] Q. M. Zhang, J. Su, C. H. Kim, R. Ting, and R. Capps, "An experimental investigation of electromechanical responses in a polyurethane elastomer," *J. Appl. Phys.*, vol. 81, pp. 2770-2776, 1997.
- [24] Z.-Y. Cheng, R. S. Katiyar, X. Yao, and A. S. Bhalla, "Temperature dependence of the dielectric constant of relaxor ferroelectrics," *Phys. Rev. B*, vol. 57, pp. 8166-8177, 1998.
- [25] J. Su, Q. M. Zhang, C. H. Kim, R. Y. Ting, and R. Capps, "Effects of transitional phenomena on the electric field induced strain-electrostrictive response of a segmented polyurethane elastomer," *J. Appl. Polym. Sci.*, vol. 65, pp. 1363-1370, 1997.



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APPENDIX 9

ELECTROMECHANICAL COUPLING FACTOR OF ELECTROSTRICTIVE P(VDF-TrFE) COPOLYMER

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Abstract - Electromechanical coupling factors of the high energy electron irradiated poly(vinylidene fluoride-trifluoroethylene)(P(VDF-TrFE)) copolymer are characterized at the quasi-static (1Hz) and high frequency resonance states. It is found that the transverse electromechanical coupling factor k_{31} of this material can reach more than 0.45. Furthermore, the result obtained from the resonance method is comparable to that from the quasi-static method.

1. INTRODUCTION

Electroactive polymers (EAP), which change shapes as an electric field is applied, can be used in many areas such as electromechanical actuators and sensors for robots, acoustic transducers for underwater navigation and medical imaging, artificial muscles and organs, fluid pumps and valves, and smart materials for vibration and noise control¹. The basic function of the EAP in these applications is to perform the energy conversion between the electric form and mechanical form. Therefore, in these applications, it is highly desirable to have an EAP with high electromechanical conversion efficiency. However, the traditional piezoelectric EAPs exhibit low electromechanical conversion efficiency, which limit their applications in comparison with the piezoelectric ceramics.² One of the issues in the development of EAP is how to improve the electromechanical coupling factors².

It should be pointed out that from an early study based on the Landau-Davonshire theory, it has been observed that at temperatures above a first order ferroelectric-paraelectric (F-P) phase transformation temperature where a polar-phase can be induced by a DC electric bias field, the electromechanical coupling factor in the polar phase can reach very high value and if neglecting the loss, the theory predicts a coupling factor of near 100%³. This result was confirmed experimentally from the ceramic

(BaSr)TiO₃ system. However, in order to produce a practical material utilizing this phenomenon for electromechanical applications, one has to overcome the problems associated with a normal first order F-P transition, that is, the transition is sharp with large hysteresis and usually does not occur at near room temperature.

Recently, in an effort to improve the electromechanical properties of P(VDF-TrFE) copolymers, we showed that P(VDF-TrFE) copolymers modified by proper high energy electron irradiation treatments exhibits giant electrostrictive strain with high elastic energy density^{4,8}. In addition, the material exhibits a relaxor ferroelectric behavior with a broad diffused phase transition peak centered at near room temperature⁴. It is interesting to examine the electromechanical coupling factors of the material and this paper reports the results from the investigation.

2. EXPERIMENTAL

The detail of the sample processing and the characterization of the longitudinal and transverse strains were discussed in earlier publications^{4,8}. In this investigation, the electromechanical coupling factors were determined by means of the quasi-static method and resonance method. Since the copolymer studied here is an electrostrictive material, in order to carry out the resonance measurement, a DC bias field is required to induce an effective piezoelectric state in the polymer. Meanwhile, the impedance measurement circuit should be protected from this high DC voltage (~1500 volts). Presented in figure 1(a) is the circuit designed and used for the measurement of the impedance of the polymer under DC bias field. The impedance of the sample is measured through a HP 4194 impedance analyzer. The geometric shape of the sample is shown in Fig. 1(b), where the electroded area does not fully cover

the sample surface in order to prevent the air break down through the edge. As will be discussed later in the paper, this un-electroded edge will have effect on the resonance measurement, especially at high DC bias fields where the elastic modulus of the polymer in the electroded area becomes much higher than unelectroded area. The thickness of the sample here is 22 μ m.

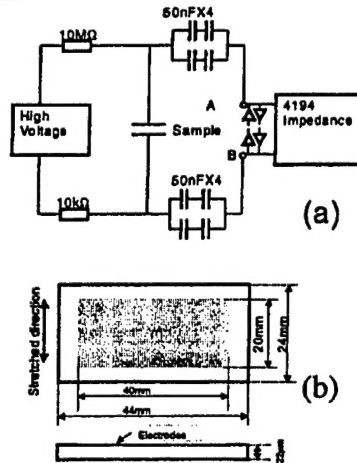


Figure 1. (a) Diagrams of the blocking circuits, and (b) Geometry of the sample for resonance measurement

3. RESULTS AND DISCUSSION

3.1 quasi-static electromechanical coupling factors

The quasi-electromechanical coupling factor k can be derived from the definition:

$$k^2 = \text{stored mechanical energy} / \text{input electric energy}$$

From the P-E polarization-field relation, the elastic modulus, and the strain-field relation, Hom et al. has derived the quasi-static electromechanical coupling factor for an electrostrictive material,⁹

$$k_{31}^2 = \frac{kS_i^2}{s_{ii}^D \left[P_B \ln \left(\frac{P_S + P_B}{P_S - P_B} \right) + P_S \ln \left(1 - \left(\frac{P_B}{P_S} \right)^2 \right) \right]} \quad (1)$$

where $i=1$ or 3, corresponding to the transverse or longitudinal direction (for example, k_{31} , is the transverse coupling factor) and s_{ii}^D is the elastic

compliance under constant polarization. For the irradiated copolymer studied here, the polarization field relationship (P-E) follows⁵

$$|P_B| = P_S \tanh(k|E|) \quad (2)$$

where P_S is the saturation polarization and k is a constant. Using Eq. (1) and Eq. (2) with the measured strain, elastic modulus, and polarization loop, the quasi-static longitudinal coupling factor k_{33} and transverse coupling factor k_{31} are calculated and presented in Fig. 2. Fig. 2(a) is the longitudinal coupling factor k_{33} for the unstretched sample. The data indicate that at near room temperature and under 80MV/m electrical field k_{33} of more than 0.3 can be achieved, which is comparable to or even higher than that obtained in single crystal P(VDF-TrFE) copolymer¹⁰, the highest value reported for this class of polymer. The data in Fig. 2(b) is the k_{31} for the stretched film along the stretching direction. The data show that a coupling factor of more than 0.45 can be obtained in the stretched copolymer, which is much higher than those in unirradiated P(VDF-TrFE) copolymers and even higher than k_{31} in most of the piezoceramics.¹¹ Since the energy conversion efficiency is proportional to the square of the coupling factor, this improvement is significant.

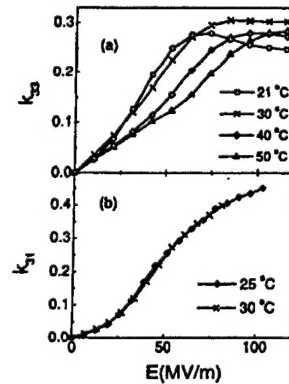


Fig. 2. The quasi-static electromechanical coupling factor vs. electrical field for the electron irradiated P(VDF-TrFE) copolymer. (a) the longitudinal coupling factor k_{33} for for unstretched P(VDF-TrFE) 68/32mol% film irradiated at 105 °C with 70 Mrad dose using 1.0 MeV electrons, and (b) the transverse coupling factor k_{31} along the stretch direction for stretched P(VDF-TrFE) 68/32 mol% film irradiated at 100 °C with 70 Mrad dose using 1.2 MeV electrons

3.2 Resonance measurement of the coupling factor

The coupling factor of a piezoelectric material can also be determined by means of the resonance method, where the electric impedance as a function of frequency is measured around the frequency of a specific resonance. Frequency dependence of dielectric behavior of the stretched and irradiated P(VDF-TrFE) copolymer is shown in Fig. 3. The data show: 1) Dielectric constant and loss decrease with DC bias field. 2) a clear resonance exists at frequency of 20~50KHz, corresponding the resonance along the sample stretching direction. 3) The resonance becomes stronger as the DC bias field increases.

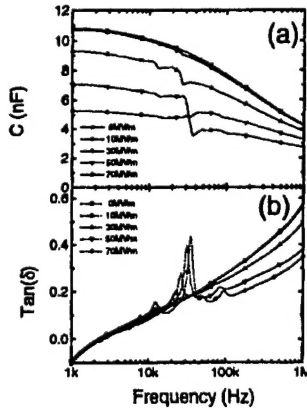


Fig. 3. The impedance as a function of frequency under different DC bias field for stretched P(VDF-TrFE) 68/32 mol% film irradiated at 100 °C with 70 Mrad dose using 1.2 MeV electrons. (a) the capacitance, and (b) the dielectric loss.

With the dielectric behavior at Fig. 3, the impedance and admittance of the sample can be calculated. From the frequency dependence of the real part (R) of the impedance and the real part (G) of the admittance, the series resonance frequency f_s , which is the frequency at the maximum R, and the parallel resonance frequency f_p , which is the frequency at the maximum G, can be obtained. The coupling factor k_{31} can be determined from

$$\frac{k_{31}^2}{1 - k_{31}^2} = \frac{\pi f_p}{2 f_s} \tan\left(\frac{\pi f_p - f_s}{2 f_s}\right) \quad (3)$$

$$C = C_0 \left\{ 1 + \frac{K[J/2 + 2P(1+K) - D][1 - \tan^2 b] \tanh(bJ/2) + K[1 - \tanh^2(bJ/2)] \tan b}{b[1 + \tan^2 b \tanh^2(bJ/2)]} \right\} \quad (4)$$

the electro-mechanical coupling effect k_{31} of the sample under difference DC bias fields is shown in Fig. 4. The coupling coefficient can reach more than 30% when 70MV/m DC-bias field is applied. The results are nearly the same as that obtained from the quasi-static case, indicating that the coupling factor of the sample does not change much with frequency.

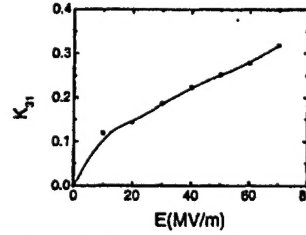


Fig. 4 Electromechanical coupling coefficient vs. dc-bias fields for the copolymer shown in Fig. 2 (b) and 3. Where point is the experimental data, and the line is the eye-guide.

For a piezoelectric material with relative high dielectric and mechanical losses, caution should be exercised when the standard resonance method is used to determine the coupling factor. A more precise means of obtaining the coupling factor from the resonance impedance curve is to directly fit the curve by explicitly taking into consideration that all the material coefficients are complex¹². Based on that, the frequency dependence of capacitance can be expressed as Eq. (4), where the complex capacitance (C^*), elastic compliance (s^*), electromechanical coupling factor (k^*), and acoustic velocity (V^*) are assumed to be: $C_0^* = C_0(1 - jD)$, $s_{11}^{E*} = s_{11}^E(1 - jJ)$, $k_{31}^* = k_{31}(1 - jp)$, $V^* = (\rho s_{31}^{E*})^{-1/2} = V(1 + j(J/2))$, respectively, and $K = k_{31}^2$, $b = 2\pi fL/2V$.

The frequency dependence of the measured capacitance around resonance frequency was fitted in terms of Eq. (4) using the least square fitting method. The typical fitted result is shown in Fig. 5 as an example for the high-energy electron irradiated P(VDF-TrFE) copolymer film under 70MV/m DC

bias field, where normalized capacitance (C/C_0-1) was used. The electromechanical coupling factor from the fitting is 31.2%, comparable to that calculated directly using equation (3).

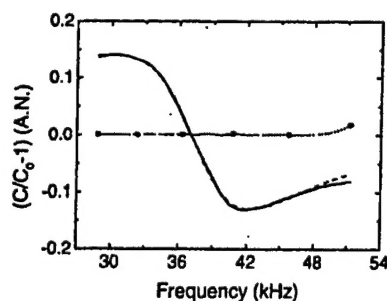


Fig. 5. Example of the fitting of the resonance curve for the high-energy electron irradiated P(VDF-TrFE) copolymer film under 70MV/m DC bias field. The solid line is the measured data, the dash line is the fitted data, and dot line with circle symbols is the fitting error.

3.3 The effect of unelectroded edges on the resonance measurement

The IEEE standard resonance method is derived for the sample geometry when the field is uniformly applied to the sample under measurement. As shown in Fig. 1(b), however, in our experiment, the electrodes do not cover the whole surface of the sample and there are small unelectroded edges in the sample which are used to prevent the electric breakdown when under high DC bias voltage (~1500 volts) since the measurement was carried out in air. This unelectroded edge area has at least two effects which make the measurement at higher DC bias field very difficult. (1) The elastic modulus of the sample increases with the DC bias field and as a result, there is a difference in the elastic modulus between the electroded sample and the unelectroded edges when a DC bias field is applied. If this difference is small, the acoustic resonance in the polymer sample still depends on the geometric parameter rather than the electrode size. However, if this difference is large, it is likely that there are resonances in the electroded area rather than the whole sample. This will make the resonance behavior very complex, as indeed been observed experimentally. (2) Because of the high electrostriction in the sample, a high DC bias field

will generate a high strain in the electroded area of the sample, while the unelectroded edges will remain in unstrained state. This will cause strong sample distortion which further complicate the resonance curve. For those reasons, the experimental data measured at DC bias higher than 70 MV/m were not analyzed.

4. Summary

The electromechanical coupling factors of the newly developed electrostrictive P(VDF-TrFE) copolymer are characterized at both low and high frequencies. At low frequency, k_{33} can reach more than 0.3, while k_{31} can reach more than 0.45. The results obtained at high frequencies (~50 kHz) are nearly the same as those at quasi-static, indicating that the coupling factor is not strong frequency dependent. This work was supported by DARPA and ONR.

REFERENCE

1. T. T. Wang, J. M. Herbert, and A. M. Glass, Editors, *The Application of the Ferroelectric Polymers* (Blackie, Chapman and Hall, New York, 1988).
2. K. Tashiro, K. Takano, M. Kobayashi, Y. Chatani, and H. Tadokoro, *Ferroelectrics*, **57**, 297 (1984); K. Tashiro, S. Nishimura, and M. Kobayashi, *Macromolecules*, **23**, 2802, (1990).
3. Q. M. Zhang, J. Zhao, T. Shrout, N. Kim, L. E. Cross, A. Amin, and B. M. Kulwicki, *J. Appl. Phys.* **77**, 2549 (1995).
4. Q. M. Zhang, V. Bharti and X. Zhao, *Science*, **280**, 2101 (1998).
5. X. Zhao, V. Bharti, Q. M. Zhang, T. Romotowski, F. Tito, and R. Ting, *Appl. Phys. Lett.* **73**, 2054 (1998).
6. Z.-Y. Cheng, T.-B. Xu, V. Bharti, S. Wang, and Q. M. Zhang, *Appl. Phys. Lett.* **74**, 1901 (1999).
7. Z.-Y. Cheng, V. Bharti, T. B. Xu, S. Wang, Q. M. Zhang, T. Ramotowski, F. Tito, and R. Ting, *J. Appl. Phys.* **86**, 2208 (1999).
8. V. Bharti, Z.-Y. Cheng, S. Gross, T. B. Xu, and Q. M. Zhang, *Appl. Phys. Lett.* **75**, 2653 (1999).
9. C. Hom, S. Pilgrim, N. Shankar, K. Bridger, M. Massuda and S. Winzer, *IEEE Trans. Ultrason. Ferro. Freq. Contr.* **41**, 542 (1994).
10. K. Omote, H. Ohigashi, K. Koga, *J. Appl. Phys.* **81**, 2760, 1997.
11. D. Berlincourt, D. Curran, and H. Jaffe, *Physical Acoustics*, Vol. I Part A, 169 (Academic Press, NY and London 1964).
12. Q. C. Xu, A. R. Ramachandran, and R.E. Newnham, *Journal of Wave-Material Interaction*, **2**(2), 105 (1987).